1966

The calculation of resonant states of atoms and molecules by quasi- stationary methods

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Monterey, California. U.S. Naval Postgraduate School

http://hdl.handle.net/10945/9452

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THE CALCULATION OF RESONANT STATES OF ATOMS AND MOLECULES BY QUASI-STATIONARY METHODS

THE CALCULATION OF RESONANT STATES OF ATOMS AND MOLECULES BY QUASI-STATIONARY METHODS

by

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A Dissertation Presented to the

FACULTY OF THE GRADUATE SCHOOL

UNIVERSITY OF SOUTHERN CALIFORNIA

In Partial Fulfillment of the

Requirements for the Degree

DOCTOR OF PHILOSOPHY

(Chemical Physics)

August 1966

UNIVERSITY OF SOUTHERN CALIFORNIA
THE GRADUATE SCHOOL
UNIVERSITY PARK
LOS ANGELES, CALIFORNIA 90007

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*under the direction of h*is *Dissertation Committee, and approved by all its members, has been presented to and accepted by the Graduate School, in partial fulfillment of requirements for the degree of*

DOCTOR OF PHILOSOPHY

DEDICATION

To my wife, Ann,
for patience, forbearance,
and silence beyond that expected of any wife.

ACKNOWLEDGMENTS

I would like to thank the United States Navy, the U. S. Naval Postgraduate School, and the Office of Naval Research for selecting me to participate in the Advanced Science Program and supporting my studies.

It is also a great pleasure to express my appreciation to Dr. Howard S. Taylor for the great amount of help, encouragement and enthusiasm which he contributed to this work.

Also, I would like to thank the University of Southern California Computer Sciences Laboratory and Administration, without whose help and lack of foresight in selection of computers and personnel this work would have been completed a year earlier, and R. J. Mackin, Jr. of the Physics Section of the Jet Propulsion Laboratory, Pasadena, California for allowing the use of the facilities of the Laboratory, in particular the computer facilities, in order that the calculations required in this work could be completed.

For many useful discussions and suggestions, I would like to thank Dr. A. Golebiewski, and I would like to thank Dr. E. Weltin for his help in revising the computer program and Dr. I. Eliezer for helping with some of the calculations.

Also, it would be impossible to conclude without expressing my appreciation to Mrs. Hope Melickian for her help in typing and proof-reading of the manuscript.

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CHAPTER I

INTRODUCTION

An important development in recent collision experiments has been the evidence of autoionizing compound negative ion states with lifetimes from 10^{-14} to 10^{-12} seconds; considerably shorter than the lifetimes of electronically excited states ($\sim 10^{-8}$ sec.). These compound states have been used to explain resonances in elastic scattering cross sections (Simpson and Fano, 1963), the onset of inelastic processes where no states of the target exist (Schulz and Philbrick, 1964; Chamberlain, 1965), forbidden transitions (Baranger and Guerjoy, 1957), and dissociative attachment (Schulz, 1958).

Most of the states observed in electron scattering experiments have energies lying slightly (0.1 - 1.0 eV) below known excited states of the target and the usual decay process is autoionization. Some specific examples of targets are hydrogen, helium, and the hydrogen molecule.

In hydrogen, the first excited state is ^2S 2s or ^2P 2p at 10.204 eV above the ^2S 1s ground state. A resonance has been observed by Schulz (1964) at 9.75 ± .15 eV, just below the 2s or 2p energy.

At 19.3 eV above the ground state of the helium atom there is a sharp He^- resonance which is so well known that it is used for energy

scale calibration (Schulz, 1964; Simpson, Kuyatt, et al., 1965a; and many others). This is just below the $^{1,3}S$ 1s2s states of helium at an average energy of 20.2 eV. Fano and Cooper (1965) have also discussed higher He^- resonances, such as the ^2P $(2s)^2 2p$ at 57.1 eV and ^2D $2s(sp)^2$ at 58.2 eV. These lie just below the ^1S $(2s)^2$ and ^3P 2s2p states at 57.9 and 58.4 eV respectively.

The pre-ionization states of helium can be considered as resonances of He^+ plus an electron. Madden and Codling (1964) have observed a set of these autoionizing levels, and Cooper, Fano and Prats (1963) have shown that they correspond to a series $(2snp+ns2p)^1P$, n = 2,3, ... which converges to He^+ 2p (or 2s) at 65.395 eV.

Kuyatt, Simpson and Mielczarek (1965b, 1966) have observed pairs of resonances starting about .9 eV below the $^{3,1}\Pi_u$ states of the hydrogen molecule, and studied the isotope effect in HD and D_2. In these experiments, spacings of levels were observed which correspond closely to the vibrational levels of the excited H_2 (HD,D_2) states, which seems to indicate that the third electron in the compound state became trapped in the field of the excited target state, but far enough away that it had little effect on the nuclear motion. Golden and Bandel (1965) report substantially the same result.

Various methods have been proposed and used for calculating the energies and wave functions of these compound states, particularly for scattering of electrons off atoms. The problem is that the normal variation method is inapplicable, as an infinity of states of the same symmetry and equal or lower energy exist for each resonance

consisting of the ground state of the target plus a free electron with the proper angular momentum and a continuum of energy values.

Fano (1961) and Burke and Schey (1962) have developed methods which actually deal with the scattering cross section. The Fano theory is particularly useful for analysis of line shape, while Burke and Schey use a close-coupling technique to calculate the cross section and study resonances as part of the total scattering problem.

Holøien (1958a,b), Holøien and Midtal (1965, 1966) Mandl and Herzenberg (1963, series), O'Malley and Geltman (1965), Taylor and this author (1965), and Lipsky and Russek (1966) have devised quasi-stationary methods for calculation of the energy and wave function of resonant states without predicting any of the features of the cross section except the approximate position of the resonance. Of the above, Taylor and Williams (1965, hereinafter denoted as TW) were the first to do calculations on systems other than two-electron atoms. The Taylor-Williams calculation was on the diatomic molecule H_2 plus an electron, and the results compared quite well with the experiments of Kuyatt, et al. (1965) and Golden and Bandel (1965). Since that time, Mandl and Herzenberg (1965) have done a parametrized calculation on the ${}^3\Sigma_u^+$ state of H_2 plus an electron with their modified Kapur-Peierls technique.

Taylor, Nazaroff, and Golebiewski (1966, hereinafter denoted as TNG), with the aid of the author, have presented a formal justification of the physical quasi-variation method of TW, and presented a complete quasi-stationary method for calculating the energy of resonances

which includes the TW method as a special case. This work also lists and classifies three types of resonances, including the examples above and two other types which will be discussed later.

Therefore, one of the aims of this work is to present the Taylor-Williams quasivariation method with its original physical arguments, and the formal justification of it as presented by TNG. This is done in Chapter II.

The second aim is to apply these methods to small diatomic molecules (in particular, H_2), calculating resonant states and comparing to electron scattering experiments (Chapter III, ff.).

Finally, in conjunction with the second aim, the diatomic molecule calculation methods of Harris (1960) Taylor and Harris (1963, series), and Taylor (1964) for bound states of six electrons or less have been revised to include the quasi-stationary methods, and have been extended to allow both bound and quasi-stationary calculations of energies and wave functions of larger diatomic systems. The latest revision, presented and discussed in the Appendices, can do calculations on up to twenty electrons.

CHAPTER II

THEORY

The formation, lifetime, and decay of the compound states mentioned above can only be described rigorously by wave packets composed of combinations of bound and continuum states of the N+1 electron system. The resonance is simply a highly localized wave packet which remains so for 10^{-14} to 10^{-12} seconds, so that with the proper restrictions, it can be treated as stationary during this time. This is similar to the treatment of electronically excited states as stationary by ignoring the light field interactions, where inclusion of the light field leads to decay in approximately 10^{-8} seconds.

Without any restrictions, a carefully executed variational calculation will lead to the conclusion that no compound states exist, since one can construct an infinite number of states of the same symmetry and equal or lower energy. Thus, even to apply the Hylleraas-Undheim procedure, treating the resonance as the m^{th} excited state, one would have to diagonalize an infinite secular determinant, taking the uppermost root as the resonance energy.

The original work of Taylor and Williams (TW, 1965) presented a quasi-variation method based on physical arguments for selecting the

proper restrictions so that valid results could still be obtained.

Briefly the method stated that if an N+1 electron bound state function could be guessed such that it nearly represented the physical situation, it would also closely resemble the proper linear combination of wave packets, and the matrix elements of interaction of this bound function with the infinite number of continuum functions would be so small compared to the bound-bound interactions that the infinite Hamiltonian matrix would be nearly numerically block diagonalized, separating the bound state in the continuum from its adjacent continuum.

The rules given for selecting these N+1 electron functions were that they must be doubly excited, autoionizing configurations, but with small autoionization probability in order to obtain long lifetimes. The small autoionization probability could be assured by selecting "weakly correlated" orbitals (i.e., orbitals having small $1/r_{ij}$ matrix elements) for the trial wave function. This choice of functions causes both the Hamiltonian and overlap matrices to be nearly block diagonal in the prescribed manner, since the double excitation produces an excited core which is orthogonal to the ground state of the target. Integration over the inner electrons will make the bound-continuum matrix elements small. Hence the total secular determinant is approximately block diagonalized into a finite part mixing multiply excited configurations of the compound state and an infinite part which can be ignored.

These arguments work quite well for certain types of resonances,

but considerable experimental evidence has appeared that there are other resonances which the quasi-variation method would not be able to calculate. Taylor, Nazaroff, and Golebiewski (TNG, 1966) analyzed the experimental data and proposed that it could be explained by three types of resonance, which they classified as Type I Core-Excited, Type II Core-Excited, and Single Particle (hereinafter denoted by CE1, CE2, and SP, respectively).

The resonances of He, H, and H_2 discussed above, which lie 0.1 to 1.0 eV below excited states of the target, are CE1. They could be formed by the virtual process of the impinging electron exciting one of the electrons of the target and becoming trapped in the slight potential well left when the excited electron moves out of its way, with a resultant binding energy of 0.1 - 1.0 eV. The CE1 resonances are the ones which can be handled by the quasi-variation method, and the excitation of one of the target electrons explains the classification Core-Excited.

The potential well can be considered as being formed by additional amount of nuclear charge that the impinging electron sees when the excited core electron moves away.

One of the examples in many textbooks (for instance Messiah, 1961, Vol. I, p. 88) is the case of virtual levels of the square well potential, in which it is shown that if the walls of the finite ($V_o = \infty$) well were made finite, "long-lived" localized wave packets (bound states in the continuum) can be formed only at those energies in the continuum of the well ($E > V_o$) at which bound states would have

existed had V_o not been reduced to a finite value.

Based on this argument, TNG proposed the existence of CE2 resonances as virtual states of the potential well caused by core excitation. These resonances should be quite broad (short lived - width is inversely proportional to lifetime) compared to CE1, since they are adjacent to the continua of both the ground state of the target and the excited state of the target, and have no binding energy to provide stability. Experimental examples cited as indicative that CE2 resonances exist were the Hg^- $(5d^{10}6s6p^2)$ $^4P_{5/2}$ seen by Kuyatt, Simpson, and Mielczarek (1965) at 4.89 eV, and an elusive peak seen by the same experimenters in the elastic scattering of electrons from helium at 21.4 to 21.6 eV, just above the n = 2 levels. Schulz and Philbrick (1965) and Chamberlain and Heideman (1965) observed a stronger peak in the inelastic cross section of He corresponding to nearly the same energy. TNG attribute this resonance to a CE2 above the n = 2 level of He, rather than a CE1 below the n = 3 level, as the necessary binding energy below the n = 3 level would indicate a longer lived resonance and therefore a narrower peak than that observed, and an electron affinity of 2 eV for the n = 3 level as opposed to .1 to .6 for the n = 2 level.

In the same spirit, it is argued that if an excited target state can support virtual levels, it should be possible for the ground state to do so also. Several experimental observations exist which cannot be explained except by postulating such states, which TNG classified as Single Particle since the physical model assumed is the

nearly unperturbed ground state plus an orbiting planetary electron. These states are also expected to be quite broad.

The experiments leading to these conclusions are the N_2 - electron scattering experiments of Schulz (1962, 1964, 1966), the H_2 - electron dissociative attachment experiment of Schulz and Asundi (1966), and structure in the elastic He - electron scattering cross section at about 0.45 eV observed by Schulz (1965).

The introduction of the CE2 and SP resonances requires a more effective procedure for calculating the energy of resonances.

TNG, with the assistance of the author, presented a stabilization method which generalizes the quasi-stationary methods mentioned above (page 3), and incorporates a way of handling CE2 and SP as well as CE1 resonances.

The methods of calculating the resonant energies are basically refinement methods. The wave function of the resonant state is written as a superposition of configurations selected on the basis of experimental results and intuition. The refinement method is used to improve the wave function by calculating correction terms. Even though this method is an approximate method, it will be justified below on formal grounds. The most direct justification of the method, however, is the fact that it allows one to calculate ab-initio very good approximations to the experimentally observed resonant energies.

In order to gain perspective it is well to consider for the moment how one might calculate an approximate wave function and energy of an excited bound state of an atom or molecule. If the state in

question is the Mth excited state of a given symmetry one might choose a large number of properly symmetrized basis functions (greater than M), diagonalize the Hamiltonian of the system and optimize the Mth root according to the Hylleraas-Undheim procedure. However, if the state is very highly excited such a procedure will in general not give a good result. One is thus forced to try other methods. There are two possible alternative approaches: a variation-perturbation method or a quasi-variation technique. In a variation-perturbation method one chooses a zero-order wave function and then corrects it by variational versions of perturbation techniques. Such perturbation methods include the inverse nuclear charge method (Knight and Scherr, 1963), the method of Kirtmann and Decious (1966) and the methods of Hirschfelder et al. (1965) and Byers Brown et al. (1966). These methods are convenient to apply if the system is not too large. For larger systems one is forced to use quasi-variational approaches in which a limited number of configurations is selected on intuitive grounds. These configurations are then optimized variationally by means of linear and non-linear parameters. In such methods one must be careful that the final wave function does have dominant those configurations which one feels on intuitive grounds should be dominant. One adds other configurations to the wave function to see if the mixing is appreciable and constantly checks whether the energy is stabilized. In other words, in practice one must use intuition to a large degree to guide the variational method towards the desired result.

All of the methods mentioned above depend for their success on

the choice of trial functions. The Hylleraas-Undheim method will give poor results if the basis set is chosen poorly; the perturbation methods will give poor or entirely wrong results if the zero-order function is not chosen properly; the quasi-variation of linear and non-linear parameters will also give poor or incorrect results if the configurations chosen do not fit the physics. In the following discussion it will be shown that the situation is much the same in resonant-state calculations.

In order to discuss resonances let us consider a scattering experiment in which a projectile is scattered by a target. The target might be a nucleus and the projectile a neutron or proton as in nuclear physics, or the target might be an atom or molecule and the projectile an electron as in electron-impact spectroscopy. Let us consider an experiment in which a beam of projectiles is fired from a gun at the target, scattered by the target and then detected in a detecter. The entrance channel is thus an incoming projectile with the target in the ground state. If the energy of the projectile is insufficient to excite the target, the scattering is elastic and the exit channel will be an outgoing projectile with the target in the ground state. Far from the scattering center (i.e. in the detector) the wave function for the total system is thus a product of the ground-state target wave function and a sum of incoming projectile waves and outgoing spherical projectile waves.

A traditional way of describing an elastic resonance in nuclear physics (Blatt and Weisskopf, 1952) is to say that at certain kinetic

energies the incoming projectile penetrates the target and forms a compound system. The compound system exists for a short time and then decays back into a target in the original state and an elastically scattered electron. The presence of the compound state is evidenced by a sharp and narrow resonance in the elastic scattering cross section at the so-called resonant energy. The possible resonant energies, i.e. the energies of the possible resonant states, are obtained by excluding the incoming and outgoing waves and solving for the energy levels of the compound projectile-target system as if it were a bound system.

One possible way of excluding the incoming and outgoing continuum contributions to the resonant wave function is to put the compound system in a box. In nuclear physics this is a reasonable procedure. The surface of the box would be the surface of the compound nucleus. Since nuclear forces are short-ranged, one can meaningfully define a nuclear surface and can partition physical space into inside the compound nucleus and outside the compound nucleus. However, in the case of electron-atom or electron-molecule scattering it is difficult to define a box because of the long-range Coulombic electron-electron forces. One achieves the effect of putting the compound system in a box by partitioning the Hilbert space of the compound-system Hamiltonian instead of physical space. The Hilbert space is partitioned into **P**-space which contains all functions expandable in terms of the asymptotic exit channels and into Q-space which contains all functions having no projection on the asymptotic exit channels. Hence, one

diagonalizes the compound-state Hamiltonian in Q-space. The solutions so obtained can have meaning only in the situation in which the electron is confined to the vicinity of the target. The electron has thus been put in a box whose radius is the range of the effective scattering potential without even specifying that radius. It will be shown formally below that diagonalizing the Hamiltonian in Q-space is equivalent to diagonalizing the pseudo-Hamiltonian $QHQ = H_{QQ}$ in the full Hilbert space. The operator Q is a projection operator which selects Q-space. The method of calculating resonances thus reduces to diagonalizing the compound-system projectile-target Hamiltonian with as large a basis set as is possible which does not include the asymptotic exit channels.

Let us consider the case of electron-atom scattering. The projectile is an electron and the target is an N-electron atom presumed to be in its ground state. The total energy of the system is the kinetic energy of the incoming electron and the ground-state energy of the atom. In order to obtain the resonant states (and energies) of the (N + 1)-electron atom one looks for apparent bound states of the (N + 1)-electron Hamiltonian in the vicinity of the experimental energy. Therefore, in order to calculate the resonant energies of the electron-atom system, one must diagonalize the full (N + 1)-electron Hamiltonian of the total system as mentioned above.

The problem which is encountered is that as mentioned above the energy of the reasonant state will not in general correspond to the lowest root of the (N + 1)-electron Hamiltonian. The situation is

thus similar to that encountered in solving for the energy of a very highly excited bound state, hence one can use either perturbation-variation or quasi-variation methods to zero in on and stabilize the desired root. In order for a root-stabilization method to work the energy of the intuitively-guessed wave function must be close to the actual resonant energy. It is only in such a case that one can safely discard any configuration which seriously alters the energy. One expects a root-stabilization method to work because the electrons most involved in the resonances cannot be highly correlated. If they were highly correlated, the resonant state would not possess a long enough lifetime to be observed experimentally. The low correlation indicates that a one-electron picture (i.e., trial function as product of one electron orbitals, or small linear combination of products) is meaningful. One therefore expects the energy of the resonant state to have essentially settled down to its final value, i.e. to have become stabilized, after mixing a few configurations with the intuitively guessed one(s).

A word of caution is necessary on the use of a stabilization method. If a root cannot be stabilized with a small number of configurations either an incorrect wave function has been chosen to start with or the basis set is not a good one. If very closely-spaced roots begin to occur, then the concept of root-stabilization becomes meaningless and the method is inapplicable. This would be the case if the resonant state belonged to a group of very closely-spaced resonant states. The desired state would be a member of a group of almost

degenerate resonant states in this case. In such a case one would have to consider all of the almost degenerate resonant states as a unit.

The quasi-variation method of Taylor and Williams (1965) and the equivalent method of O'Malley and Geltman (1965) can now be seen to be incomplete. In these methods the Q-space was constructed by eliminating from the basis set all configurations containing those target states included in the exit channels, i.e. they eliminated all parent target states lying below the resonant state. Therefore, these methods could not be used to calculate single-particle or type II core-excited resonant states because they lie above their parent target states. These methods do give results for core-excited type I resonant states comparable with experiment since the core-excited resonant states do not involve to a large degree the lower lying parent target states. Because of the small correlation between the extra electron and the target, the ground target states do not mix very strongly. In other words, the quasi-variation method is a way of zeroing in on the root for those resonant states in which the wave function does not include appreciable overlap with the initial target states (i.e. those target states occurring in the exit channels). The Q-space of the quasi-variation method is a subspace of the more general Q-space of the stabilization method.

The obvious fault of the stabilization methods is that they do not calculate lifetimes. One could stabilize, especially in the case of a single-particle or type II core-excited resonant state, on a root corresponding to a resonant state which is too short-lived to be

observed experimentally. The perturbation method will definitely calculate such short-lived resonant states if the choice of zero-order wave function forces it to do so. In the case of type I core-excited resonant states we are confident that the lifetimes are of the order of 10^{-14} to 10^{-13} seconds. For single-particle of type II core-excited resonant states experience and intuition are not well enough developed to allow even rough estimates.

Now that the quasi-stationary methods have been described, it remains to show that the eigenfunctions and eigenvalues they yield do correspond to resonant states. In this section the Feshbach theory of resonant reactions (1958, 1962) will be used to establish this correspondence by showing that eigenfunctions of $QHQ = H_{QQ}$ do lead to a Breit-Wigner form in the cross section and correspond to a decaying bound state.

The equation to be solved is the (N + 1)-electron Schrödinger equation for the projectile-target system

$$H\Psi\left(\underline{r}_1,\underline{r}_2,\cdots,\underline{r}_{N+1}\right) = E\Psi\left(\underline{r}_1,\underline{r}_2,\cdots,\underline{r}_{N+1}\right) \qquad (1)$$

for a given energy E. The operator H is the full Hamiltonian of the system and $\Psi\left(\underline{r}_1,\underline{r}_2,\cdots,\underline{r}_{N+1}\right)$ is the total wave function. The procedure used by Feshbach (1962) is to partition space with two projection operators P and Q such that they satisfy the relationships

$$P\Psi\left(\underline{r}_1,\underline{r}_2,\cdots,\underline{r}_{N+1}\right) \xrightarrow[1 \leq i \leq N+1]{r_i \to \infty} \Psi\left(\underline{r}_1,\underline{r}_2,\cdots,\underline{r}_{N+1}\right) \qquad (2)$$

and

$$
\begin{aligned}
P + Q &= 1 \\
P^2 = P, \ Q^2 &= Q \qquad (3) \\
PQ = QP &= 0
\end{aligned}
$$

The projection operator P projects out of the wave function all components on the available asymptotic exit channels at the given energy E.

The Schrödinger equation, Eq. (1) can now be solved formally in a way which will show the resonances explicitly. Writing $\Psi = Q\Psi + P\Psi$ Feshbach partitioned Eq. (1) into a set of two coupled equations

$$\left(H_{PP} - E\right) P\Psi = -H_{PQ} Q\Psi \qquad (4a)$$

and

$$\left(H_{QQ} - E\right) Q\Psi = -H_{QP} P\Psi \qquad (4b)$$

where $H_{PP} = PHP$, etc. Solving Eq. (4b) for $Q\Psi$ and inserting the result into Eq. (4a) yields

$$\left(H_{PP} + H_{PQ} \frac{1}{E - H_{QQ}} H_{QP}\right) P\Psi = EP\Psi \qquad (5a)$$

or

$$\left(H_{PP} + V_{opt}\right) P\Psi = EP\Psi \qquad (5b)$$

where V_{opt} is the optical potential. In order explicitly to introduce the resonances into the picture one must consider the equation

$$\left(H_{QQ} - \epsilon_n\right) \phi_n = 0 \quad . \qquad (6a)$$

If this equation has eigensolutions, they must be eigenfunctions of Q with eigenvalue unity, i.e., $Q\phi_n = \phi_n$, and Q can be expanded in terms of its eigenfunctions as

$$Q = \sum_n |\phi_n\rangle\langle\phi_n| \tag{6b}$$

where the summation includes the integral over the continuum if necessary. Inserting this expression into V_{opt} yields

$$\left(H_{PP} + \sum_n \frac{H_{PQ}|\phi_n\rangle\langle\phi_n|H_{QP}}{E - \epsilon_n}\right)P\Psi = EP\Psi \tag{7}$$

Therefore, the optical potential has poles at energies equal to the eigenvalues of Eq. (6). In the case of well-separated resonances one can break up the optical potential into two parts when E is near one of the ϵ_n, say ϵ_s. Thus, Eq. (7) may be rewritten as

$$\left(H_{PP} + \sum_{n\neq s} \frac{H_{PQ}|\phi_n\rangle\langle\phi_n|H_{QP}}{E - \epsilon_n} - E\right)P\Psi = -\left(\frac{H_{PQ}|\phi_s\rangle\langle\phi_s|H_{QP}}{E - \epsilon_s}\right)P\Psi \tag{8a}$$

or, by definition of H′,

$$(H'-E)P\Psi = -\left(\frac{H_{PQ}|\phi_s\rangle\langle\phi_s|H_{QP}}{E - \epsilon_s}\right)P\Psi \ . \tag{8b}$$

The operator H′ is that part of the Hamiltonian which varies slowly with the energy E and gives rise to non-resonant scattering while the operator $H_{PQ}|\phi_s\rangle\langle\phi_s|H_{QP}/E-\epsilon_s$ gives the rapidly changing, or resonant, contribution to the scattering.

The first step in solving Eq. (8b) is to solve the homogeneous portion $(H'-E)P\Psi_0^{\pm} = 0$, where the + indicates that the solution

satisfies outgoing boundary conditions and minus indicates that the solution satisfies incoming boundary conditions. The functions $P\Psi_o^{\pm}$ describe non-resonant scattering since they are associated with H'. It is assumed that $P\Psi_o^{\pm}$ exist and are known. Given the set of ϕ_n from Eq. (6) and $P\Psi_o^{\pm}$ one can investigate the T matrix (see Goldberger and Watson, 1964) and thus the scattering cross section. From the outgoing homogeneous solution $P\Psi_o^+$ a Green's function can be constructed and an integral equation for the total outgoing solution $P\Psi^+$ can be derived, namely

$$P\Psi^+ = P\Psi_o^+ + \frac{1}{E^+ - H'} \frac{H_{PQ}|\phi s\rangle\langle\phi s|H_{QP}|P\Psi^+\rangle}{E - \epsilon_s} \tag{9}$$

Operating on the left with $\langle\phi s|H_{QP}$ on both sides of Eq. (9) one finds the relation between $\langle\phi s|H_{QP}|P\Psi^+\rangle$ and $\langle\phi s|H_{QP}|P\Psi_o^+\rangle$ which, after substitution back into Eq. (9), allows one to write $P\Psi^+$ as

$$P\Psi^+ = P\Psi_o^+ + \frac{1}{E^+ - H'} \frac{H_{PQ}\;|\phi s\rangle\langle\phi s|\;H_{QP}|P\Psi_o^+\rangle}{E - \left(\epsilon_s + \Delta^{(s)}\right) + \frac{1}{2}\,i\Gamma^{(s)}} \tag{10}$$

where, using Feshbach's notation,

$$\Delta^{(s)} - \frac{1}{2}\Gamma^{(s)} = \langle\phi s|H_{QP}\frac{1}{E^+ - H'}H_{PQ}|\phi s\rangle \tag{11}$$

Since the inverse operator $1/E^+ - H'$ can be written as

$$\frac{1}{E^+ - H'} = \mathcal{P}\left(\frac{1}{E - H'}\right) - i\pi\,\delta(E - H') \tag{12}$$

the explicit definitions of the energy shift $\Delta^{(s)}$ and the level width $\Gamma^{(s)}$ are

$$\Delta^{(s)} = \langle\phi s|H_{QP}\,\mathcal{P}\left(\frac{1}{E - H'}\right)H_{PQ}|\phi s\rangle \tag{13}$$

and

$$\Gamma^{(s)} = 2\pi \langle \phi_s | H_{QP} \delta(E-H') H_{PQ} | \phi_s \rangle \tag{14a}$$

or, equivalently, using the expansion $H_{PQ}|\phi_s\rangle = \int a(E')|P\Psi_o^+(E')\rangle dE'$

$$\Gamma^{(s)} = 2\pi |\langle \phi_s | H_{QP} | P\Psi_o^+(E_s)\rangle|^2 \tag{14b}$$

The T matrix for the effective Schrödinger equation (8b) is

$$\langle \chi_o | T | \chi_o \rangle = \langle \chi_o | V | P\Psi^+ \rangle \tag{15}$$

where χ_o is the eigenfunction of that part of H', called H_o, which describes unperturbed motion of the incident particle and target system, that is H_{pp}, and where according to Eq. (8) V is given by

$$V = V_{\substack{\text{non-resonant}\\ \text{potential}}} + \left(\frac{H_{PQ}|\phi_s\rangle\langle\phi_s|H_{QP}}{E - \epsilon_s} \right)_{\substack{\text{resonant}\\ \text{potential}}} \tag{16}$$

Inserting $P\Psi^+$ from Eq. (10) into Eq. (15) and recalling that $P\Psi_o^+$ is the outgoing non-resonant scattering solution of $(H' - E)P\Psi_o^+ = 0$ and therefore satisfies

$$P\Psi_o^{\pm} = \chi_o + \frac{1}{E^{\pm} - H_o} (H' - H_o)\, P\Psi_o^{\pm} = \left[1 + \frac{1}{E^{\pm} - H'} (H' - T_o) \right] \chi_o \tag{17}$$

it is seen after some manipulation (see Goldberger and Watson, 1964, sec. 5.4)

$$\langle \chi_o | T | \chi_o \rangle = \langle \chi_o | H' - H_o | P\Psi_o^+ \rangle_{\text{non-resonant}}$$

$$+ \left(\frac{\langle P\Psi_o^- | H_{PQ} | \phi_s \rangle \langle \phi_s | H_{QP} | P\Psi_o^+ \rangle}{E - \left(\epsilon_s + \Delta^{(s)}\right) + \frac{1}{2} i\Gamma^{(s)}} \right)_{\text{resonant}} \tag{18}$$

Since the cross section is proportional to the square of the T matrix, it will show a Breit-Wigner form and will change rapidly at $E \approx \epsilon_s + \Delta^{(s)}$ with a half-width of $\Gamma^{(s)}$. When E is not near $\epsilon_s + \Delta^{(s)}$ the non-resonant term will dominate and the cross section will vary smoothly with the energy.

Thus with a rigorous formalism applicable to both atomic and molecular cases it has been shown that the eigenfunctions of the effective Hamiltonian H_{QQ}, Eq. (6), do indeed lead to rapid changes of the Breit-Wigner type in the scattering cross section when the energy E is near an eigenvalue of H_{QQ}. It is assumed that H_{QQ} does have bound-state solutions in the vicinity of the energy E. If this is not the case, the resonant term will obviously vanish at that energy.

In order to interpret what is happening physically when a resonance occurs it is necessary to form a wave packet centered about the energy E. To determine with good precision the time at which the particle enters the "internal region," where $Q\Psi$ is non-zero, a sharp wave packet involving a broad range of energies ΔE must be constructed with the assumption that $\Delta E \gg \Gamma$. Choosing t = 0 as the time at which the incident particle enters the internal region, the part of the packet due to the $Q\Psi^+$ part of Ψ^+ at t = 0 may be written as

$$Q\Psi(\underline{r},t) = \int_{\Delta E} C(E)\, Q\Psi^+(E)\, e^{-iEt}\, dE \tag{19}$$

where C(E) is a slowly varying function of energy. From the

expression

$$Q\Psi = \frac{1}{E^{+} - H_{QQ}} H_{QP} \; P\Psi^{+} \qquad (20)$$

it can be shown that, for E near ϵ_s, one has

$$Q\Psi(\underline{r}) \approx \frac{\frac{1}{2}\sqrt{\frac{2}{\pi\Gamma^{(s)}}}\,\Gamma^{(s)}}{E - \left(\epsilon_s + \Delta^{(s)}\right) + \frac{1}{2}\, i\Gamma^{(s)}} \, \phi_s(\underline{r}) \qquad (21)$$

To see this one has to introduce the operator Q (in Eq. (6b)) before the H_{QP} operator in Eq. (20) and the expression (10) for $P\Psi^{+}$, and select all resonant terms of the resulting expression which have the factor $1/E^{+} - \epsilon_s$. In the final step one has to replace $\langle \phi_s | H_{QP} | P\Psi_o^{+} \rangle$ by its absolute value (changing in this way only the phase factor of ϕ_s) and to realize that according to Eq. (14b) $|\langle \phi_s | H_{QP} | \Psi_o^{+} \rangle| = \sqrt{\Gamma^{(s)}/2\pi}$. Therefore at t = 0, $E \approx \epsilon_s$

$$Q\Psi(\underline{r},0) \approx \int_{\Delta E} C(E) \frac{\frac{1}{2}\sqrt{\frac{2}{\pi\Gamma^{(s)}}}\,\Gamma^{(s)}}{\left(\epsilon_s + \Delta^{(s)}\right) - E - \frac{1}{2}\, i\Gamma^{(s)}} \, \phi_s(\underline{r}) \; dE \; . \qquad (22)$$

At time t this internal wave function becomes (since $\Psi^{+}(E)$ are eigen-functions of H)

$$Q\Psi(\underline{r},t) \approx C\left(\epsilon_s + \Delta^{(s)}\right)\phi_s(r) \int_{\Delta E} \frac{\frac{1}{2}\sqrt{\frac{2}{\pi\Gamma^{(s)}}}\,\Gamma^{(s)} e^{[-iE/\hbar]t}}{\left(\epsilon_s + \Delta^{(s)}\right) - E - \frac{1}{2}\, i\Gamma^{(s)}} \, dE \qquad (23)$$

the assumption being made that ΔE is broad compared to the resonance at $\epsilon_s + \Delta^{(s)}$, but small compared with the distance between successive

resonances. With the usual approximations for sharply peaked integrands, the integration limits may be extended to $-\infty$ and $+\infty$ yielding

$$Q\Psi(\underline{r},t) \approx \frac{1}{2}\sqrt{\frac{2}{\pi\Gamma^{(s)}}}\,\hbar\Gamma^{(s)}\,C\left(\epsilon_s + \Delta^{(s)}\right)\,\phi_s(\underline{r})$$
$$\times \int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega t}}{\left[\left(\epsilon_s + \Delta^{(s)}\right) - \frac{1}{2}\,i\Gamma^{(s)}\right] - \hbar\omega} \tag{24}$$

This familiar integral (in time-dependent perturbation theory) can be evaluated to give (see Goldberger and Watson, chapter 8)

$$Q\Psi(\underline{r},t) = \begin{cases} \sqrt{\frac{2}{\pi\Gamma^{(s)}}}\;\pi\, i\Gamma^{(s)}\, C\left(\epsilon_s + \Delta^{(s)}\right)\phi_s(\underline{r}) & \\ \quad\times\, e^{-i/\hbar(\epsilon_s+\Delta^{(s)})t}\, e^{-\Gamma^{(s)}/2\hbar\, t} & t > 0 \\ 0 & t < 0 \end{cases} \tag{25}$$

The $Q\Psi$ part of the wave packet thus comes into effect as the particle comes into the region of the target. In this region the $Q\Psi$ part of the packet and thus the N+1 electron system resembles a stationary eigenfunction of H_{QQ} except for the fact that this "stationary" state is modulated and decreased in time by an exponential decay factor with mean lifetime $\tau = h/\Gamma^{(s)}$. It has therefore been shown that the N+1 particle system does exist as a quasi-stationary localized state for an average time τ. If one looks at Messiah's development of radiation theory, (1963) where projection operators are used to separate the light field from the matter states, one sees that the use of the word

"stationary" in describing the states of negative ions is either rigorous or approximate in the same sense that one calls "stationary" any excited state of an atom or molecule that has a finite spontaneous emission probability.

The beauty of the projection operator formalism is its generality. It does not depend on the choice of H, and Q and P are only required to satisfy $P\Psi \rightarrow \Psi$ at large distances, so that the formalism can be applied to any decaying state problem. Note, however, that both the formal theory and the quasi-stationary methods require that the physical situation be inserted, either by chemical intuition or by proper choice of the projection operators P and Q. This is the price which must be paid for not being able to integrate the Schrödinger equation exactly.

CHAPTER III

RESONANT STATES OF H_2^-*

Introduction

In this paper the quasivariation method developed simultaneously by Taylor and Williams (1965, hereinafter denoted by TW) and O'Malley and Geltman (1965), and the stabilization method discussed in the work of Taylor, Nazaroff, and Golebiewski (1966, hereinafter denoted by TNG) are applied to the *ab initio* calculation of quasi-stationary states of H_2^-. Results are compared quantitatively and qualitatively to dissociative attachment, vibrational excitation and electron scattering experiments.

For the definitions of, and distinctions between the three types of resonance calculated here (Single Particle and Core-Excited Types I and II, hereinafter denoted by SP, CE1, and CE2, respectively); the usefulness of these definitions and a discussion and derivation of the variational principles used in the present work, see the paper of TNG.

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*This chapter is to be submitted verbatim to the Journal of Chemical Physics for publication under the joint authorship of James K. Williams and H. S. Taylor.

Experiments and Results

The experiments simplest to explain with the calculations presented here are those in which resonances are seen in the total and inelastic electron-hydrogen cross section. Such observations have been made by Kuyatt, Simpson and Mielczarek (1964, 1965b, 1966) in transmission experiments, by Golden and Bandel (1965) with a modified Ramsauer technique and by Heidemann, Kuyatt, and Chamberlain (1966) in inelastic scattering experiments. These resonances are attributed to the formation of two short-lived states of H_2^-, and the individual peaks in the cross section correspond to definite vibrational levels of the resonant molecular state. The well-developed vibrational structure indicates a lifetime sufficiently long for molecular vibrations of the order of 10^{-13} sec.[1]

As was noted in all publications on these resonances, there is a striking resemblance of the vibrational spacings of the two resonances themselves, and also of the spacings of the resonances and the spacings of the four H_2 states $c^3\Pi_u$, $a^3\Sigma_g$, $C^1\Pi_u$ and $E^1\Sigma_g$.

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[1] In the earliest of their publications, Kuyatt et al. report only one resonant state. They later refined the experiment to observe two close-lying states. In TW, a rough calculation was carried out which agreed with the one resonance observed at that time. The general results of TW are still valid but are superseded by the more detailed calculations and analysis of this work. In this work, comparisons will be made with the later experiments of Kuyatt et al., which differ somewhat in energy scale from those of Golden and Bandel. This is admittedly done because of better agreement of the calculations with the Kuyatt work.

This indicates, as discussed in TNG, that the observed resonances are CE1, an electron in the field of a mixture of the four H_2 states above. Based on physical arguments, TW correctly credited the first resonance to a $^2\Sigma_g\ \sigma_g 1s\pi_u 2p_{+1}\pi_u 2p'_{-1}$ configuration of H_2^-, i.e., an electron in the field of the $^3\Pi_u$ state.[2]

The possible configurations that result from addition of an excited orbital to the four H_2 states and could cause resonances are listed in Table 1. Non-autoionizing configurations are omitted. In the third section, the details of the mixing of those configurations with the same symmetry in both the quasivariation and stabilization methods are reported.[3]

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[2] Since we are using open shell calculations, a prime is used to indicate an orbital of slightly larger average radius than the unprimed orbital. The orbital notation is the standard Mulliken LCAO notation and is used for simplicity of presentation. Any particular Mulliken orbital can be thought of as the dominant term in an expansion of the molecular orbitals, used in this paper and explained in a later section, upon a complete set of Mulliken orbitals.

[3] Only the two $\sigma_g 1s\pi_u 2p_{+1}\pi_u 2p_{-1}'$ resonances and a portion of curve D of Fig. 1 were calculated with the quasivariation method as well as the stabilization method. The latter was used for all other H_2^- states. The reason for this is the difficulty encountered in orthogonalization of the wavefunction of the resonance to the wavefunctions of the states of H_2 of lower energy whenever the main configuration(s) has two orbitals which are not of π type. This orthogonalization is a requirement of the quasivariation method, but is not required when the stabilization method is used. The difficult orthogonality requirement will probably mean that most future calculations will be done by the stabilization method. Added to this difficulty in the quasivariation method is the fact that CE2 and SP resonances can only be calculated by the stabilization method, as discussed in TNG.

TABLE 1

SOME POSSIBLE H_2^- RESONANT STATES

H_2^-		Parent H_2 States
$^2\Sigma_g$	$\sigma_g 1s \pi_u 2p_{+1} \pi_u np_{-1}$	$c^3\Pi_u$, $C^1\Pi_u$
$^2\Pi_u$	$\sigma_g 1s \pi_u 2p_{+1} \sigma_g 2s$	$c^3\Pi_u, a^3\Sigma_g^+, C^1\Pi_u, E^1\Sigma_g^+$
$^2\Sigma_g^+$	$\sigma_g 1s(\sigma_g 2s)^2$	$a^3\Sigma_g^+, E^1\Sigma_g^+$
$^2\Delta_g$	$\sigma_g 1s(\pi_u 2p)^2$	$c^3\Pi_u, C^1\Pi_u$

Fig. 1.--Potential curves for H_2^- resonances and some associated H_2 states.

A - H_2^- $^2\Sigma_g^+$ consisting of $C^1\Pi_u \cdot \pi_u 2p'$

B - H_2^- $^2\Sigma_g^+$ consisting of $c^3\Pi_u \cdot \pi_u 2p'$

C - H_2^- $^2\Sigma_g^+$ consisting of $B^1\Sigma_u^+ \cdot \sigma_u 1s'$

D - H_2^- $^2\Sigma_g^+$ consisting of $^3\Sigma_u^+ \cdot \sigma_u 1s'$

E - H_2^- $^2\Sigma_u^+$ consisting of $X^1\Sigma_g^+ \cdot \sigma_u 1s$

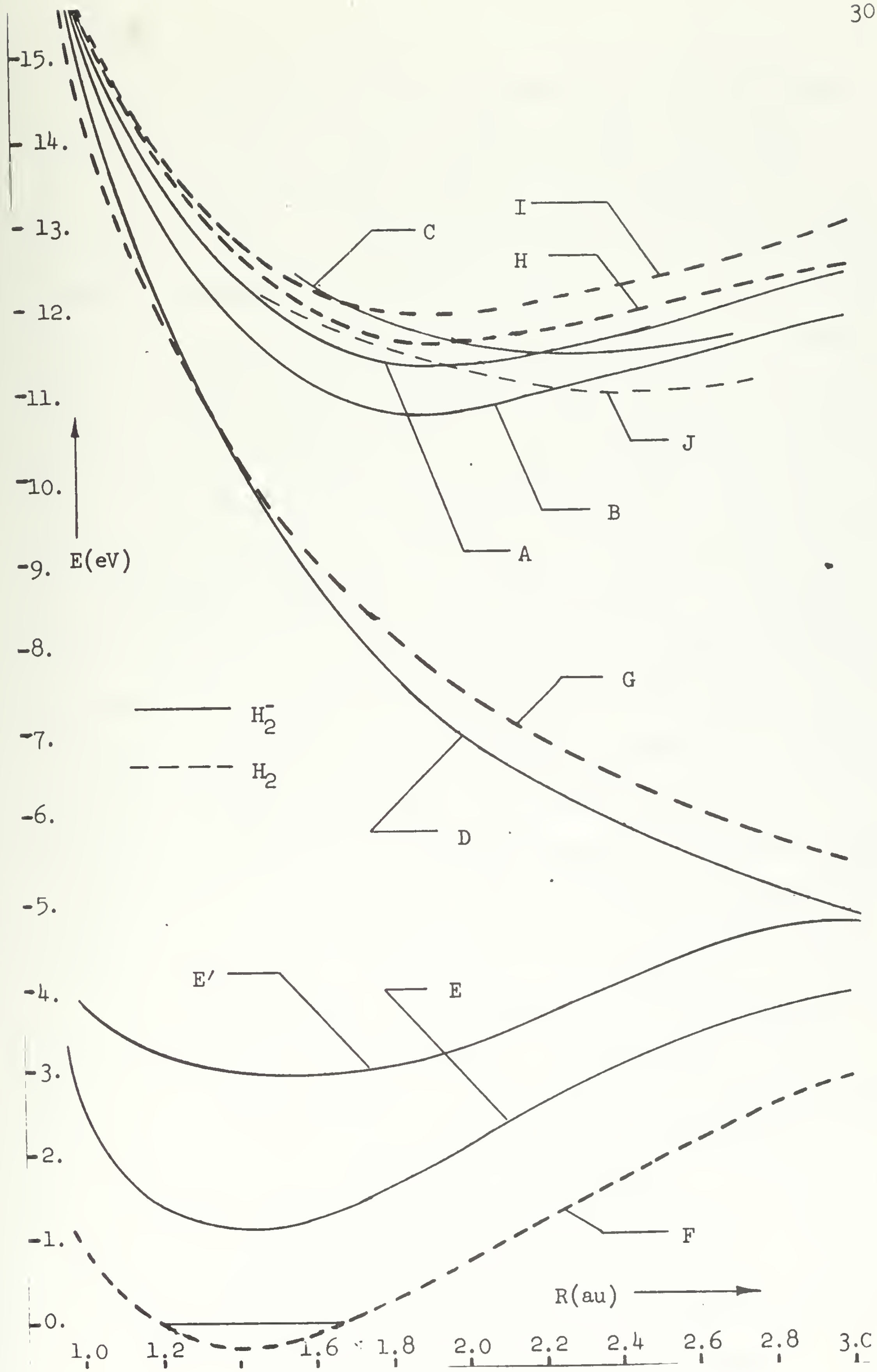
F - H_2 $X^1\Sigma_g^+$ (Kolos and Wolniewicz, 1965).

G - One configuration result for H_2 $^3\Sigma_u^+$ $1\sigma_g 1\sigma_u$. This curve lies about 0.32 eV above the "exact" $^3\Sigma_u^+$ curve (Kolos and Wolniewicz, 1965), but is used as a comparison with the H_2^- calculation consisting of this configuration plus an extra electron.

H - Two configuration result for H_2 $^3\Pi_u$ $(1\sigma_g 1\pi_u + 1\sigma_u 1\pi_g)$. The minimum of this curve lies about 0.14 eV above the experimental minimum. The H_2 $a^3\Sigma_g^+$ curve lies so close to this one that they are indistinguishable on this scale.

I - Same as H for $C^1\Pi_u$ and $E^1\Sigma_g^+$

J - H_2 $B^1\Sigma_u^+$



15.
14.
13.
12.
11.
10.
9.
8.
7.
6.
5.
4.
3.
2.
1.
0.
E(eV)
I
H
C
J
B
A
G
D
E'
E
F
H_2^-
H_2
R(au)
1.0
1.2
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0

The outstanding result of the present calculation for these two resonances was that the lower resonance is almost exclusively $^3\Pi_u$ + e, $^2\Sigma_g^+$ $\sigma_g 1s\pi_u 2p_{+1}\pi_u 2p_{-1}'$ while the next resonance is $^1\Pi_u$ + e, $^2\Sigma_g^+$ $\sigma_g 1s\pi_u 2p_{+1}\pi_u 2p_{-1}'$. In Table 2, the vibrational levels of these two states are compared to the observed levels of Kuyatt et al., and good agreement is obtained. The calculation also demonstrated a number of physical effects which were discussed in TNG. First, it was found that even though the two CE1 $\sigma_g 1s\pi_u 2p\pi_u 2p'$ states were mixed with themselves, with all the states of the same symmetry $^2\Sigma_g^+$ in Table 1, and with many configurations of non-stable H_2^- states of lower energy, the ratios of the off-diagonal elements of the Hamiltonian matrix to the diagonal elements were $\mathcal{O}(10^{-6})$ or less between the two spin doublets themselves, and between each of the spin doublets and the large number of other H_2^- configurations. This indicates the expected extremely weak interactions (low correlation) between electrons in the compound state. The electron affinity of the lower CE1 resonance is 0.8488 eV relative to its parent $^3\Pi_u$ state, and the higher CE1 resonance has 0.8435 eV binding relative to its $^1\Pi_u$ parent, or 0.276 eV relative to the $^3\Pi_u$.

CE1 resonances were not attainable from configurations representing an electron in the field of the other H_2 states in Table 1. No extensive search was made in this work for CE2 resonances belonging to the states of Table 1, although to check for their existence, one good stabilization calculation was done at the equilibrium internuclear separation of the four parent states (R = 1.95 au, 1 au = .52917 Å), for the configuration an electron in the field of $^3\Sigma_g^+$; $^2\Sigma_g^+\sigma_g 1s\sigma_g 2s\sigma_g 2s'$.

TABLE 2

COMPARISON OF EXPERIMENTAL
AND CALCULATED VIBRATIONAL LEVELS
(energies in eV)

Lower Resonance				Upper Resonance			
Obs. Level	Splitting	Calc. Level	Splitting	Obs. Level	Splitting	Calc. Level	Splitting
11.28		11.07		11.46		11.46	
	.28		.30		.26		.29
11.56		11.37		11.72		11.75	
	.28		.29		.27		.28
11.84		11.66		11.99		12.03	
	.27		.27		.28		.28
12.11		11.93		12.27		12.31	
	.26		.26		.26		.27
12.37		12.19		12.53		12.58	
	.25		.24		.24		.26
12.62		12.43		12.77		12.84	
	.24		.22		.20		.25
12.86		12.65		12.97		13.09	

This root stabilized at an energy of -.72911 au (1 au = 27.21 eV), 0.24 eV above $3\Pi_u$, .3 eV below $^1\Pi_u$, .13 eV above $^3\Sigma_g$, and 11.85 eV above the ground vibrational level of $H_2X^1\Sigma_g^+$, the reference zero level for all the calculated and experimental results. This root strongly indicates the existence of a CE2 resonance with this configuration which parallels its $^3\Sigma_g^+$ parent with a slightly higher energy in the Franck-Condon region.

Again this $\sigma_g 1s\sigma_g 2s\sigma_g 2s'$ configuration does not mix with any of the $\sigma_g 1s\pi_u 2p\pi_u 2p'$ types and the resonance is expected to be quite broad relative to the CE1 resonances as discussed in TNG. It is likely that this resonance will only be observable in inelastic scattering experiments leading to its parent, however it is possible that threshold structure will obscure the observation. Because the two CE1 resonances are made from excited H_2 orbitals, it is to be expected that these resonant states are more strongly coupled to excited state exit channels of H_2, and this accounts for the enhanced signal due to these resonances in elastic scattering (see Heidemann, Kuyatt, and Chamberlain, 1966).[4]

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[4] In the next section, an even more tentative CE2 resonance, with the configuration of an electron in the field of $E^1\Sigma_g^+$, $^2\Sigma_u^+\sigma_g 1s\sigma_g 2s\sigma_u 2s$ is reported. The uncertainty of this resonance causes us to discuss it only in the next section, but it is mentioned here in the realization that many readers may not be interested in the detailed discussion of the calculations. Work is now in progress on this and other CE2 resonances expected to lie in this energy region. We emphasize that the two CE1 resonances and the single point at 11.85 eV are definitively stabilized and therefore represent final results.

In Fig. 2 the two CE1 resonances and the four aforementioned states of H_2 are shown, as well as the single point for the CE2 resonance (denoted by a cross). The solid lines represent the H_2^- CE1 resonances, the dashed lines the H_2 states, and the dotted line through the cross is the postulated potential curve of the CE2 resonance.

The next type of experiment to be discussed is dissociative attachment. The measured cross sections for the formation of the H^- ion in the process

$$e + H_2 \rightarrow (H_2^-) \rightarrow \begin{cases} H + H^- \\ H^* + H^- \end{cases}$$

are given in Figs. 3 and 4. In an as yet unpublished private communication, Dowell and Sharp have reported finding additional structure in the 8-12 eV peak. Besides the general Gaussian shape and the dip in the cross section at 11.2 eV, they have found a new series of dips on the high energy side of the peak, which have the feature of being spaced analogously to the spacings of the vibrational levels Kuyatt et al. found in their lower CE1 resonance. In TNG, it was shown how these experiments could be used to completely and definitively predict the position of the resonance potential curve causing such structural features as contained in the 8-12 eV peak. First, the general Gaussian shape, kinetic energy analysis, and isotope effect could be caused, as a result of Franck-Condon factors, by any repulsive resonant state with a potential curve which enters the Franck-Condon region of the ground vibrational level of the H_2 ground state at about 8 eV on the right, leaves it at about 13 eV on the left, and goes to the known

Fig. 2.--Comparison of the upper core-excited resonances to H_2.

A - H_2 $c^3\Pi_u$

B - H_2 $C^1\Pi_u$ and $E^1\Sigma_g^+$

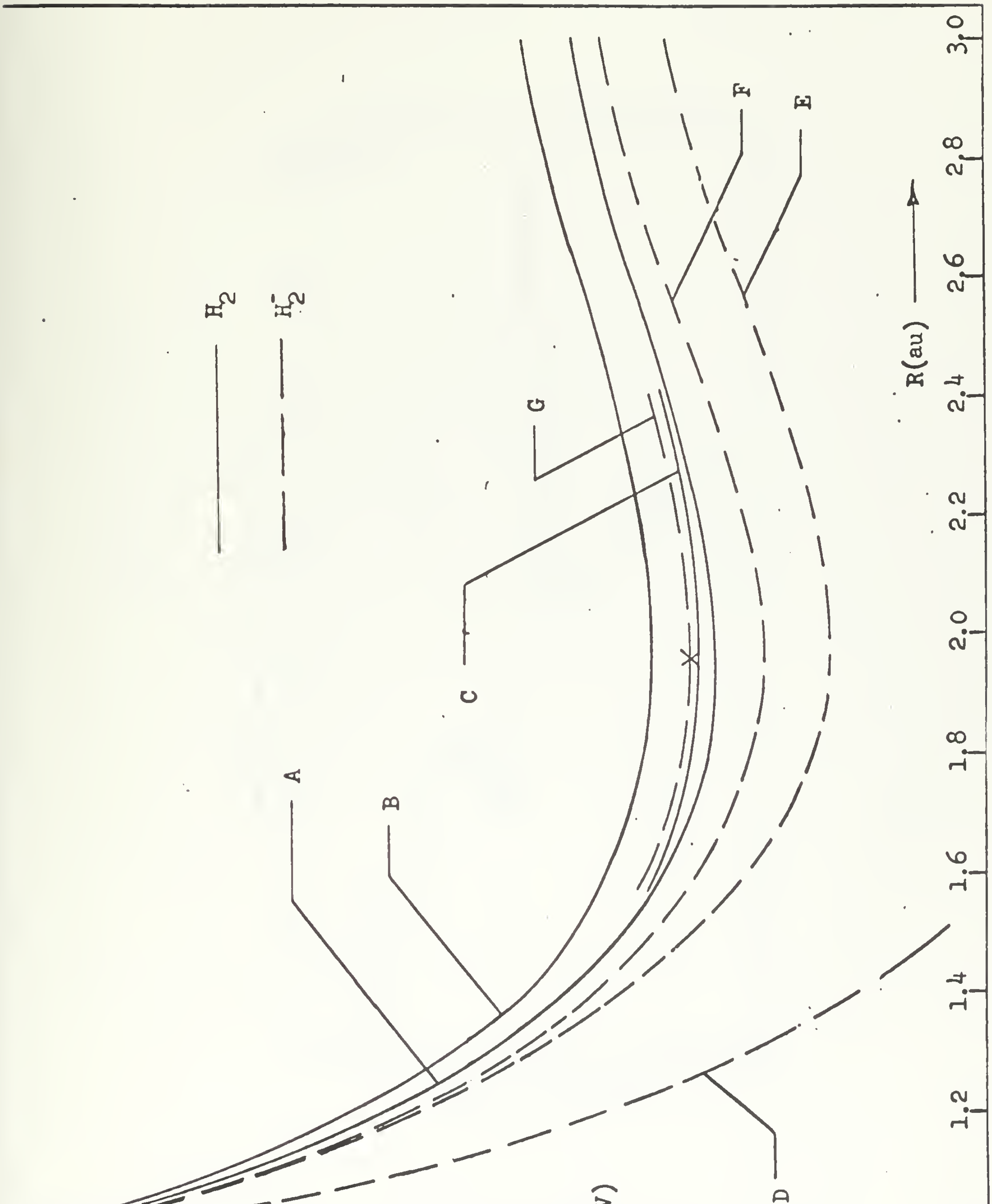
C - H_2 $a^3\Sigma_g^+$

D - H_2^- $^2\Sigma_g^+$ $\sigma_g 1s\sigma_u 1s\sigma_u 1s'$

E - H_2^- $^2\Sigma_g^+$ $\sigma_g 1s\pi_u 2p\pi_u 2p'$ ($^3\Pi_u$ + electron)

F - H_2^- $^2\Sigma_g^+$ $\sigma_g 1s\pi_u 2p\pi_u 2p'$ ($^1\Pi_u$ + electron)

G - H_2^- $^2\Sigma_g^+$ $\sigma_g 1s\sigma_g 2s\sigma_g 2s'$ ($^3\Sigma_g^+$ + electron)



E(eV)
R(au)
H2
H2-
A
B
C
D
E
F
G
16.
15.
14.
13.
12.
11.
10.
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0

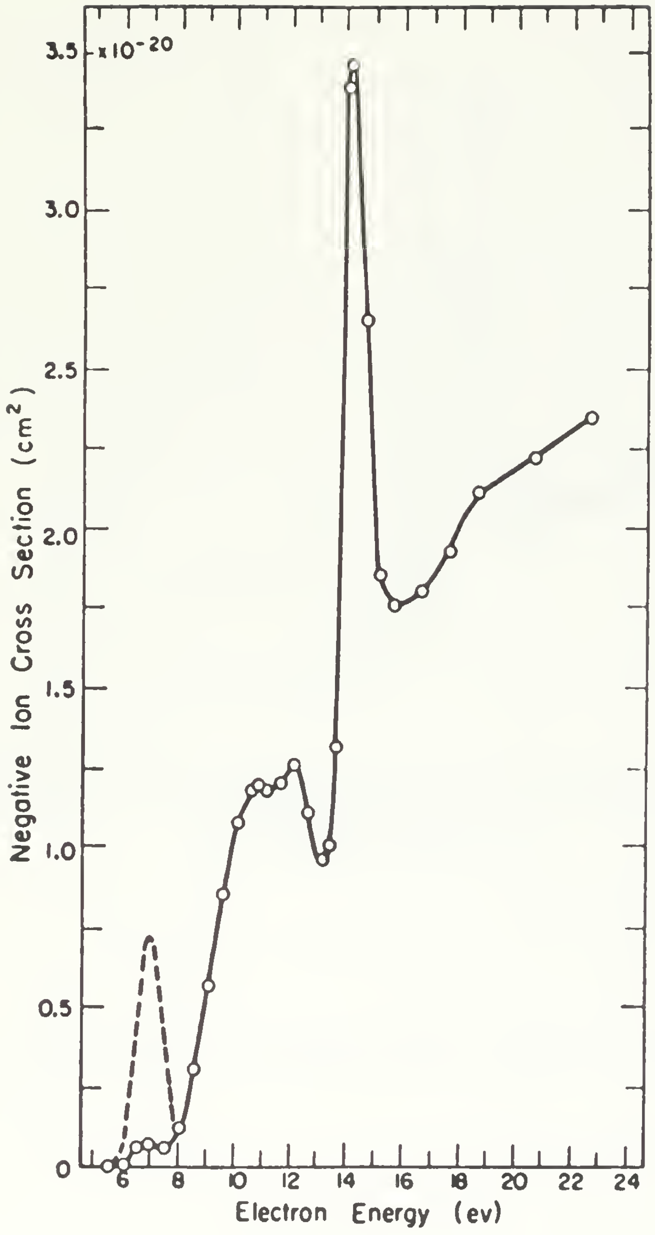


Fig. 3.--The dissociative attachment cross section of Schulz (1964).

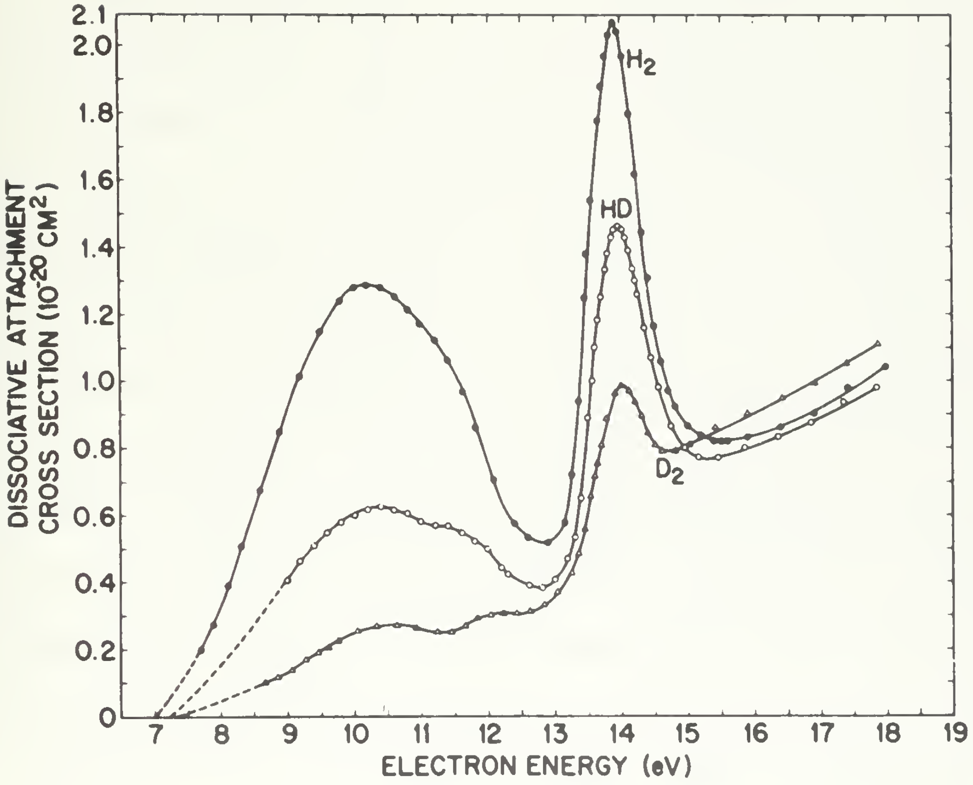


Fig. 4.--The dissociative attachment cross section of Rapp, Sharp, and Briglia (1965).

stable separated atoms H and H^- at an energy of 3.75 eV. The dip at 11.2 eV was most easily explained by assuming that this repulsive resonance potential curve could cross the repulsive H_2 $^3\Sigma_u^+$ state at 11.2 eV,[5] thereby changing from a CE1 to a CE2 resonance, and opening a new exit channel H + H + e to the system. Since, from the work of Kolos and Wolniewicz (1965), it is known that the H_2 $^3\Sigma_u^+$ state has a relative energy of 11.2 eV at $R \sim 1.29$ au, it can be concluded that the H_2^- has the same energy at this R.[5] The opening of the new exit channel causes more of the H_2^- resonances formed at this energy to decay in channels other than that measured by dissociative attachment, and therefore causes a decrease in the cross section exactly at 11.2 eV. The reason that the cross section recovers its Gaussian envelope is illustrated in Fig. 5, where it is seen that only at the crossing point are the Franck-Condon factors of sufficient magnitude to make possible curve jumping to the $^3\Sigma_u^+$ + e channel.

The Dowell and Sharp result could most simply be explained by assuming that the resonance curve proceeds upward in energy until it approaches the lower $^2\Sigma_g^+ \sigma_g 1s \pi_u 2p \pi_u 2p'$ CE1 resonance of Kuyatt et al. tangentially from the left. As shown in Fig. 6, if this were to occur, since both states are $^2\Sigma_g^+$, one could get an inverse pre-dissociation from the repulsive H_2^- state to the bound H_2^- state at energies equal to

---

[5]Actually, in order to have the maxima of the nuclear wave functions coincide, the crossing would occur at a slightly lower energy, as shown in Fig. 5. As a consequence, the R value for the crossing point predicted by the dip will be slightly smaller than the actual R value at crossing.

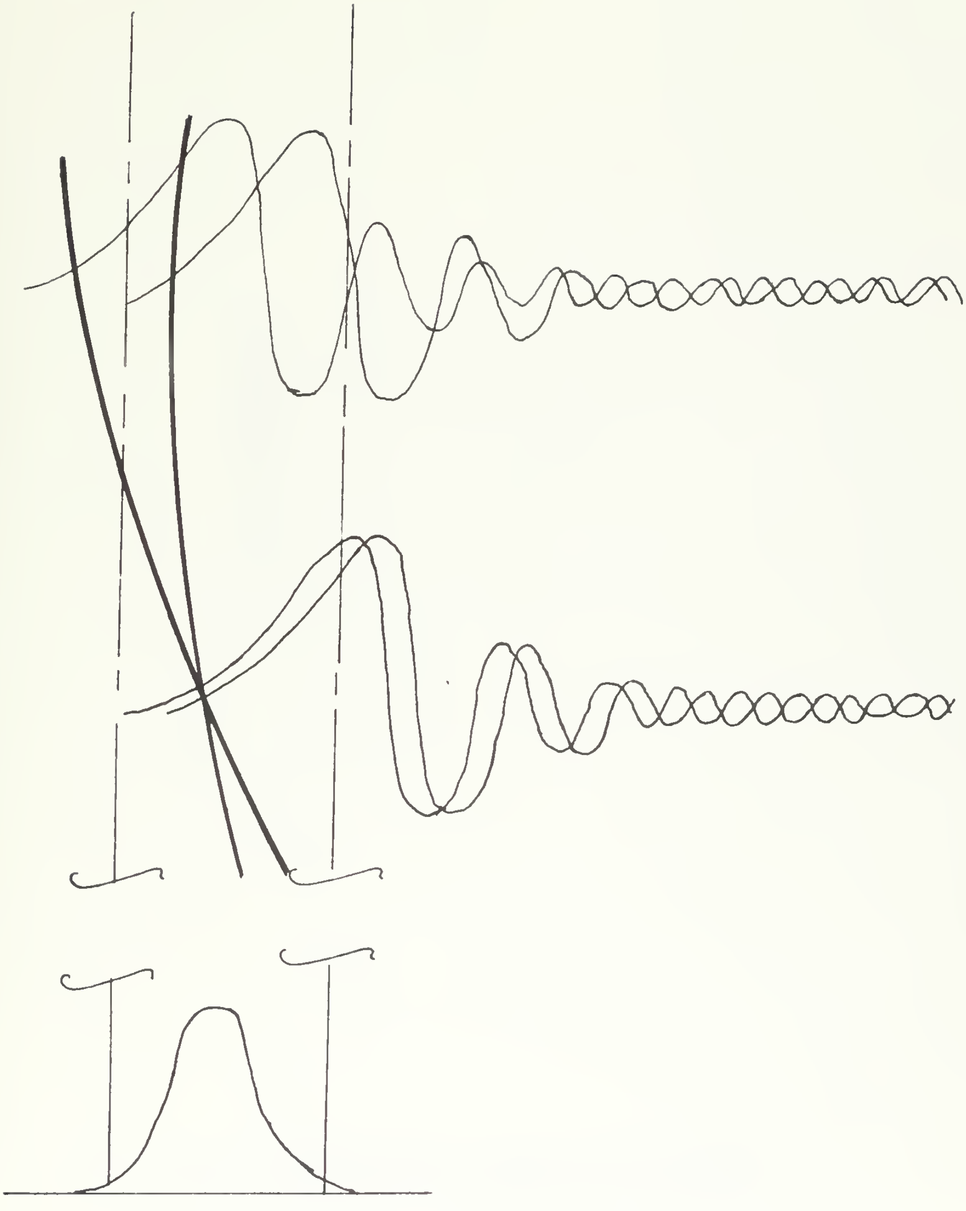


Fig. 5.--Comparison of Franck-Condon Factors.

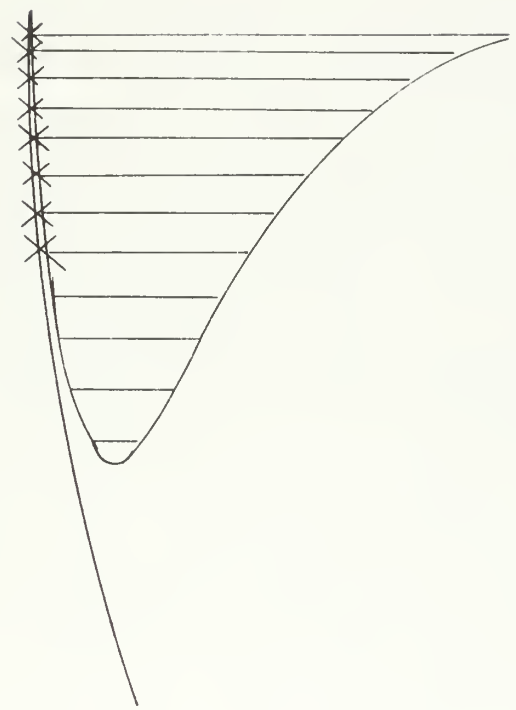


Fig. 6.--Schematic diagram for inverse pre-dissociation between resonances.

the vibrational levels of the upper resonance. Because of Franck-Condon factors (see Fig. 6) the postulated inverse pre-dissociation could only occur at vibrational levels of the upper resonance, and this could cause exactly the dips in the H^- formation cross section observed by Dowell and Sharp.

Since from experiment one knows the vibrational constants of the Kuyatt state, its potential curve can be determined empirically and the vibrational levels drawn in. By noting the energies and positions at which the vibrational levels and the empirical potential curve intersect, and by ignoring those points which do not correspond to dips in the Dowell and Sharp experiment, one is left with a set of points (denoted by crosses in Fig. 6) through which the repulsive resonance potential curve must pass. If one now smoothly connects the "cross" points of Fig. 6; the point on the H_2 $^3\Sigma_u^+$ curve; the point at which the 8 eV constant energy line intersects the large R, vertical Franck-Condon line; and the point at infinite R for the known $H + H^-$ energy, a curve (such as curve D of Fig. 1) is obtained with little ambiguity. In TNG, a conglomeration of tentative calculational, group theoretical, curve crossing and physical arguments were given to predict the curve, which, it was then pointed out, could explain the experiments. The opposite point of view is now being stressed, that once the type of phenomena that can occur in quasi-stationary molecular resonances are understood, and these are quite closely analogous to normal spectroscopic phenomena (i.e., dissociation, inverse pre-dissociation, pre-dissociation, etc.), one can predict where the resonant

state lies completely from experiment.

As also explained in TNG, simple Mulliken type arguments can be combined with the core-excited model to predict a configuration for the resonance of $^2\Sigma_g^+ \sigma_g 1s\sigma_u 1s\sigma_u 1s'$. In this work, using the stabilization method, the energy of such a configuration was calculated, and the results which are presented in Fig. 1, curve D and in Table 3 are in perfect agreement with the curve one would anticipate from the application of spectroscopic ideas to the experimental results. As will be shown in detail in the following section, this state also had extremely low correlation, since it did not mix appreciably with any configurations which would normally be regarded as correlating configurations in the configuration interaction picture. Some mixing did occur with the stabilizing configurations, particularly in the CE2 portion of the curve, indicating that the CE2 will have a larger width (be less stable) than the CE1 part. Again it is stressed that it is the lack of correlation in the resonance complex that enables the wavefunctions determined by quasi-stationary methods to give such good agreement for the energies at which resonant phenomena occur.

Work is presently in progress which will use the wavefunctions determined in this work for the $^2\Sigma_g^+ \sigma_g 1s\sigma_u 1s\sigma_u 1s'$ state in conjunction with the formal theory of dissociative attachment and vibrational excitation as developed by O'Malley (1966) and Bardsley, Herzenberg, and Mandl (1966a,b) in the hope that this will lead to quantitative agreement with experiment for dissociative attachment and will explain why Schulz is unable to observe any evidence of the $^2\Sigma_g^+ \sigma_g 1s\sigma_u 1s\sigma_u 1s'$

TABLE 3

POTENTIAL CURVES OF H_2^- RESONANCES

R(au)	E(eV)[g]					
	a	b	c	d	e	f
1.05	2.15/3.72	14.4560	--	15.0315	15.0777	--
1.1	--	13.6693	--		--	--
1.2	1.41/3.22	12.5762	--	13.5654	13.6108	(17.15)
1.3	--	11.6103	--	12.8656	12.9403	(16.15)
1.4	1.22/3.04	10.6805	--	12.3197	12.4764	(15.88)
1.5	--	9.9254	12.742	11.8956	12.0941	--
1.65	1.37/3.03	9.0085	--	11.1802	11.6621	(14.49)
1.8	--	7.9560	11.896	11.0513	11.5439	(14.14)
1.95	--	7.0404	11.735	10.9090	11.4084	
2.1	--	6.9013	--	11.0405	11.4489	
2.25	--	6.3362	11.651	11.1115	11.6084	
2.4	--	5.8157	11.577	11.3615	11.8119	
2.7	--	5.4015	11.901	11.6609	12.1744	
3.0	3.87/4.90	4.8494	--	11.9949	12.4990	
				14.12	14.12	(13.92?)

a - ${}^2\Sigma_u^+ \left(X^1\Sigma_g^+ + e,\ \sigma_g\sigma_g'\sigma_u\right)$

b - ${}^2\Sigma_g^+ \left({}^3\Sigma_u^+ + e,\ \sigma_g\sigma_u\sigma_u'\right)$

c - ${}^2\Sigma_g^+ \left(B^1\Sigma_u^+ + e,\ \sigma_g\sigma_u\sigma_u'\right)$

d - ${}^2\Sigma_g^+ \left(c^3\Pi_u + e,\ \sigma_g\pi_u\pi_u'\right)$

e - ${}^2\Sigma_g^+ \left(C^1\Pi_u + e,\ \sigma_g\pi_u\pi_u'\right)$

f - ${}^2\Sigma_u^+ \left(E^1\Sigma_g^+ + e?,\ \sigma_g\sigma_g'\sigma_u\right)$

g - energies relative to ground vibrational level of H_2 $X^1\Sigma_g$

resonance in electron impact experiments where the cross section for excitation from the ground vibrational level of H_2 to excited vibrational levels is measured. Since the resonance potential curve does cross and go above the $^3\Sigma_u^+$ channel in the Franck-Condon region, and thus lies very close to the H_2 state in the center of the Franck-Condon region, it is unlikely in any case that transitions through this resonance would make significant contributions to the vibrational excitation cross section to the lower H_2 vibrational levels.

The shape, isotope effect, and kinetic energy analysis of the 14.2 eV peak were explained in detail in TNG, and credited to transition to the dissociation limit of the two CE1 $^2\Sigma_g^+\sigma_g 1s\pi_u 2p\pi_u 2p'$ resonances discussed above. The calculations presented here reinforce and are in complete agreement with the TNG arguments hence the arguments will not be repeated here. In a future paper, the wavefunctions calculated for these states as a function of internuclear distance will also be used in conjunction with the formal theories of dissociative attachment mentioned above.

It was postulated in TNG that the vibrational excitation results of Schulz (1964) and the dissociative attachment cross section, kinetic energy distribution, and sudden onset for the peak occurring at 3.75 eV (Schulz and Asundi, 1966) could be explained by the existence of what must be a quite broad SP resonance with the configuration $^2\Sigma_u\sigma_g 1s\sigma_g 1s'\sigma_u 1s$, a $\sigma_u 1s$ electron in the field of $H_2X^1\Sigma_g^+$.[6]

[6]The reader is referred to TNG for a discussion of why this configuration was chosen; why it is expected to be broad; why the resonance is difficult to observe in transmission, mocified Ramsauer, and

The stabilization method has been applied for this state. A good ground state H_2 function was chosen, i.e., a three configuration, well correlated function which gave an energy at the minimum of the potential curve of -31.76 eV as compared to the experimental energy of -31.975 eV. The three configurations used were $\sigma_g 1s \sigma_g 1s'$; $\sigma_u^c 1s \sigma_u^c 1s'$; and $\pi_u^c 2p_{+1} \pi_u^c 2p'_{-1}$. The first configuration gives the main contribution around equilibrium nuclear separation R_e. The second is an axially correlating configuration near R_e and ensures proper breakup into two H atoms as $R \to \infty$, where it becomes as important as the $\sigma_g 1s \sigma_g 1s'$ configuration. The $\pi_u^c 2p \pi_u^c 2p'$ is an angular correlation configuration. The superscript c is added to these orbitals to indicate that they have the same average radial extent as the $\sigma_g 1s$ orbital, and are specially optimized to produce the best H_2 ground state, as opposed to the $\sigma_u 1s$ and $\pi_u 2p$ orbitals of the previous discussion which are similar to large excited orbitals of H_2.

For the ${}^2\Sigma_u$ H_2^- calculation a third electron $\sigma_u 1s$ was added to these configurations to give three three-electron configurations of symmetry ${}^2\Sigma_u^+$. This was then stabilized as discussed in the next section and resulted in the curve E of Fig. 1, as shown in detail in Fig. 7 and tabulated in Table 3. It is notable that even though one needs at least three configurations to represent this resonance well it is only because one must represent the target H_2 state to a high degree of accuracy. This type of configuration mixing does not

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[6] total cross section experiments; and the general physics of the situation.

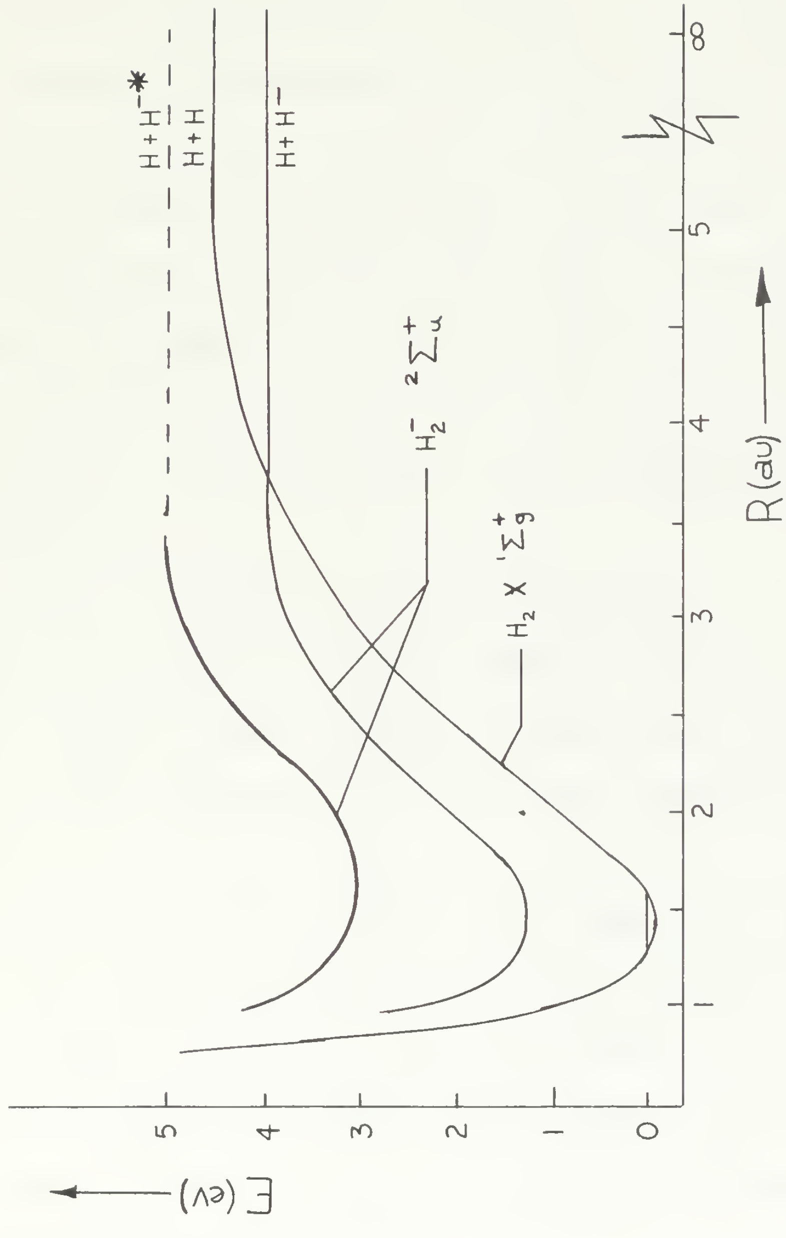

Fig. 7.--The single particle H_2^- $^2\Sigma_u^+$ states.

indicate strong correlation between the new electron and the original H_2 electrons. On the other hand, it was found that some configuration mixing was necessary before the root stabilized. This situation is analogous to that of the CE2 portion of the $^2\Sigma_g\, \sigma_g 1s\sigma_u 1s\sigma_u 1s'$ repulsive resonance, and again the extra mixing with the stabilizing configurations indicates that this resonance is quite broad. In any case, one finds a wavefunction with a small number of configurations whose eigenvalue was unaffected by further variations of the wavefunction. How much of this configuration interaction is due to width, and how much is due to a limited orbital functional form is impossible to tell.

The interesting features of this resonance are:

i) That at large R it connects smoothly to the H + H^- $^2\Sigma_u^+$ state calculated by Taylor and Harris (1963) using a true variation method since at large R H + H^- is the bound, lowest state of $^2\Sigma_u^+$ symmetry.

ii) That the potential curve for this state, once inside the curve for H_2 X $^1\Sigma_g^+$, essentially parallels the H_2 curve from above, and turns up sharply at R$\sim$1.0 au. Since its shape is like that of H_2 its harmonic vibrational constant will be similar to H_2, and thus the lower vibrational levels will be at $\sim$ 1.5 and 2.0 eV above the ground vibrational level of H_2 X $^1\Sigma_g^+$.

The calculated state could well account for the dissociative attachment result of Schulz and Asundi (1966), but it should be pointed out that the dissociative attachment experiment in this case

gives no information about the position of the potential curve for the resonance inside the target H_2 potential curve.

From the vibrational excitation experiment, Schulz (1964) postulated the existence of a very broad resonance about 2.3 eV above the ground level of H_2 X $^1\Sigma_g^+$. The result presented here is certainly lower than this. The only significant test of the calculated state that could be carried out, but for physical reasons, one which might not be extremely sensitive to the detailed form of the wavefunction, is to put the wavefunction calculated here into the formulae for the vibrational excitation cross section as presented by Bardsley, Herzenberg, and Mandl (1966a,b). This has been done by the latter authors using a wavefunction of significantly poorer quality than the one presented here[7] and nevertheless resulted in a calculated cross section which is in quite acceptable agreement with the observed one.

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[7]To demonstrate this point, one need only note that the Herzenberg et al. wavefunction gives rise to an H_2^- energy of -30.44 eV and an equilibrium internuclear separation of 1.68 au. The wavefunction used in this work, gives an energy of -31.76 eV and an equilibrium separation of 1.4 au. The "experimental" values are -31.975 eV at 1.4011 au (Kolos and Wolniewicz, 1965). Because of the different qualities of the wavefunction and the wide variations in R_e, it is meaningless to try to compare the results of the present H_2^- SP calculation with that of Herzerberg et al. Although one does not have a variation principle which says the lower the energy the better the function in these calculations, it is reasonable to assume that the more extensive and better functions used here will lead to more reliable results. The agreement with experiment in the Kuyatt et al. resonances, and the ability to explain the fine structure due to the repulsive resonance, which is completely lacking in the Herzenberg et al. results, seem to substantiate these claims.

In this laboratory the Herzenberg et al. calculations for the vibrational excitation cross section are being repeated with improved wave functions to see how sensitive the calculation is to the quality of the function.

The qualitative comparison of this state to the energy of Schulz is quite difficult since the SP state is so broad. In fact, in the vibrational excitation experiments, since the resonance is so broad, the nuclei do not have time to make definitive molecular vibrations, and Schulz was not able to distinguish any meaningful energies to determine the empirical potential curve for this stake.

When the ${}^2\Sigma_u^+$ (H_2 X ${}^1\Sigma_g$) σ_u1s root was being stabilized, it was noted that a second root stabilized equally as well. The curve for this is E′ in Fig. 1, and the upper H_2^- curve of Fig. 7. It seems to dissociate to H + H^{-*} where H^{-*} is probably the very broad H^- resonance 1s 2s calculated by Herzenberg and Mandl (1963) to have an energy between 2.0 and 4.0 eV and a width of about 2 eV. This H_2^- state, again, will be very broad, and cannot be seen in a dissociative attachment experiment since a long-lived negative ion is necessary. As discussed in TNG, because of its breadth it also might be extremely difficult to detect in the total scattering cross section. Since it occurs at about 3 eV it could possibly contribute to vibrational excitation. One might speculate that both the 1.2 eV and 3.0 eV SP resonances contribute to give the broad vibrational excitation peak estimated by Schulz to be centered at 2.3 eV. Nothing definitive can be until calculations of widths and the vibrational excitation cross section have been made.

An interesting effect observed in these SP calculations was that the extra electron of the higher stable root had a smaller effective orbital radius than that of the lower root at small R ($\sim R_e$), but at large R the situation became reversed.

When stabilizing the repulsive $^2\Sigma_g \sigma_g 1s\sigma_u 1s\sigma_u 1s'$ state, in the calculations reported here, because of the open shell methods in which two spin doublets are used, a configuration $^2\Sigma_g \sigma_g 1s\sigma_u 1s\sigma_u 1s'$ (electron in the field of $B^1\Sigma_u^+$) was automatically included. During the stabilization process, a second root corresponding to this configuration also stabilized, and it was clearly a broad, CE2 resonance. This resonance, as in the other CE1 and CE2 cases, was well stabilized and highly uncorrelated and fits the rules given in TW and TNG for a resonance in the field of the B state. It should be difficult to observe for a number of reasons. As discussed in TNG, the breadth of this resonance favors its being looked for in inelastic experiments to vibrational levels of its parent B state. However, besides its breadth, the large R_e of ~ 2.45 au and the small ω_e of ~ 0.13 eV indicate that the resonance potential curve will be in such a position relative to the potential curve of the H_2 ground state that Franck-Condon factors will allow transitions only to the highly excited vibrational levels of the resonance ($v \sim 14$) and any structure may be obscured by the closeness of the spacings. It is impossible to tell from the published curves of Heideman, et al. (1966) whether there is any structure just above the excitation threshold, and since the width is not known, it is impossible to really argue whether or not such structure should indeed be observable.

The stabilization of this root, which fits the CE model of TW and TNG, brings up a very interesting and unanswered question; it seems that in the case of core-excited resonances a well stabilized root appears fastest whenever a configuration is used which puts the extra electron into the same type of orbital as the excited H_2 orbital [e.g., $\sigma_g(\sigma_u)^2$ and $\sigma_g(\pi_u)^2$]. Other configurations do not stabilize rapidly. Why this is so, we do not know, and it is freely admitted that the extent of calculational experience so far is not sufficient to say definitely that these other configurations do not stabilize, but there are strong indications that this is the case. Another strange effect arises when one adds many configurations solely for the purpose of testing the stability of a particular root. If the root under investigation is one which is truly stable, two or three stabilizing configurations are usually sufficient. On the other hand, other roots of the secular equation do eventually become constant after large numbers of configurations have been added, simply because the configurations made of orbitals which can mix with the configurations corresponding to these roots have been exhausted. A subject of future research, especially when reliable widths can be produced, will be a study of the significance of these more slowly stabilizing states. The authors stress that the states reported in the present work stabilized rapidly, and the confusion exists only about other less stable roots which were noted in the calculations.

In the tables and graphs the energies are reported in electron volts relative to the experimental ground vibrational level of H_2 in the ground state. When energies of resonances relative to energies of

H_2 are reported, the H_2 energies are those obtained with the same wave function as for H_2^- with the exception that the linear coefficients are re-optimized and the third electron is allowed to go to infinity. This is the only way to get a true comparison and does not yield misleading results since the wavefunctions used in the H_2 case give well over 99% of the total energy and an appreciable fraction of the correlation energy. In view of the experimental errors reported, improving the calculation of resonance and target energies to a degree of sophistication comparable to that of Kolos and Wolniewicz (1965), would do little to improve our understanding of the basic physics, and therefore would not justify the many man-hours and computer expenses involved.

A point of great interest arises when discussing the non-crossing rule of quantum chemistry. As noted by Bardsley et al. (1966), and the present authors, many unstable potential curves cross the stable potential curves. This would seem inadmissable by group theoretical arguments which say that the correct potential curves must be drawn by connecting the n^{th} lowest root at all R. These arguments have meaning in the variation method, but not, however, in the quasi-stationary methods used here. Bardsley et al. show this by reference to the work of Mandl (1966) in which it was proven that for resonant states calculated by the quasi-stationary complex energy Siegert method, the real part of the energy can cross (and this is what is calculated here) but that there is no crossing in the complex plane. While the authors have no argument with this correct interpretation, we prefer to present a more physically based model. To be specific, consider the

$^2\Sigma_g^+\sigma_g 1s\sigma_u 1s\sigma_u 1s'$ repulsive resonant state, which at large R dissociates to H and H^-. This separated atom pair in turn lie about 1.0 eV below a pair H and H^{-*}, where the H^{-*} represents a SP resonance of H^- discussed by Herzenberg et al. The upper pair also has the symmetry $^2\Sigma_g^+$, but is $\sigma_g 1s\sigma_g 1s'\sigma_g 2s$.

In the united atom limit, the $^2\Sigma_g^+\sigma_g 1s\sigma_u 1s\sigma_u 1s'$ state goes to an obviously core excited state of He^-, while the H and H^{-*} pair goes to He^- $^2S(1s)^2$ 2s. The latter is clearly a very broad SP state of He^- and lies significantly lower than the core-excited state (about 19 eV). This means that the rapidly stabilizing $\sigma_g 1s\sigma_u 1s\sigma_u 1s'$ root and the unstable $\sigma_g 1s\sigma_g 1s'\sigma_g 2s$ root, which are mixed to test the stabilization of the former, should cross at a reasonably large internuclear distance. This is exactly what was observed in the calculation. The solution to this dilemma is to realize that curve crossing is a dynamical as well as a group theoretical problem, and that the nuclear motion will thus follow the diabatic curve (wave function envelope) as opposed to the adiabatic curve (energy envelope) whenever the velocity of the nuclei is significant and the electronic interactions between the two wavefunctions corresponding to the crossing curves is insignificant. In the case of core-excited resonances, it has already been pointed out several times that the mixing between the stable and added stabilizing configurations is 5-10 orders of magnitude smaller than the diagonal energy elements. (As discussed in TNG this fact is physically obvious and fundamentally the reason for the success of the quasi-stationary methods.) This means that in the problems considered here, the

diabatic curves are the ones which must be compared to experiment. The general procedure, therefore, is to follow the diabatic curves which can easily be chosen by studying the smooth change of wavefunction as a function of R, and then by looking to see if there is any significant mixing when two diabatic curves cross. A note of caution is in order — in processes like dissociative recombination and associative ionization, which are basically resonance processes, but where the relative kinetic energy of the nuclei is never more than $\sim .03$ eV at 300°K, one should follow the adiabatic curves. (A simplification is introduced in these problems, since the SP states are no longer resonances, but singly excited states of the system formed when an electron is added to the positive molecular ion, and therefore amenable to the quasivariation or variation methods.) In borderline cases, one will have to either refer to the theory of curve crossing, use Mandl's complex energy theorems, or hopefully, resolve the question unambiguously by comparison to experiment (one of the choices, diabatic or adiabatic, should give conspicuously poor agreement).

In this section any discussion of widths has been knowingly omitted. For the ${}^2\Sigma_u^+ \sigma_g 1s \sigma_h 1s' \sigma_u 1s$ SP and ${}^2\Sigma_g^+ \sigma_g 1s \sigma_u 1s \sigma_u 1s'$ repulsive state, the widths have been calculated by Herzenberg et al., but for reasons that will be discussed in a future publication, the authors

reserve judgment as to their validity.[8]

It is clear for CE1 resonances that narrowness of width greatly favors the simplification introduced by using quasi-stationary methods, as opposed to pure close-coupled scattering calculations, when one only wishes to have information about the resonances' energy, width, and assignments. For CE2 and SP, which are quite broad [lifetimes of $\mathcal{O}(10^{-14})$ sec or less][9] some authors would prefer to treat the phenomena associated with these states by pure scattering methods, especially the method of distorted waves. Herzenberg et al., in their calculation of the vibrational excitation cross section, stress that they obtain results with quasi-stationary methods for SP resonances[10] which are in as good agreement with experiment as the result of Takayanagi (1965) which was achieved with a distorted wave method.

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[8] The widths of resonances as calculated by complex energy methods similar to those used by Herzenberg et al. will be discussed in a publication in preparation by H. Taylor and A. Golebiewski. It will be shown there that the calculation of widths gives ambiguous results when the boundary enclosure (see Herzenberg et al.) is varied unless extremely large basis sets are used in the inside region. No calculations have ever been done using the complex energy method for widths in which extensive basis sets were used. Such calculations are in progress at this laboratory, and will be the subject of future communications.

[9] Single Particle resonances are expected to be even broader because of the relatively lower polarizability of the ground state.

[10] Various authors use the following names for what are denoted here by CE2 and SP: Shape resonances, virtual resonances, potential resonances, direct resonances, etc.

As pointed out by Herzenberg et al., this indicates that the two alternate models approach the true situation, that of a distorted target and an interacting passing electron, from two different limiting points of view.

The resonance formulation envisions a quasi-stationary state which must be coupled with outgoing waves, while the distorted wave method envisions a polarized target and a distorted orbit for the passing electron. Both of these approximations, if refined, will of course give the same result.

One can certainly say that the resonance formulation allows one to carry over the chemical concepts that are well known in spectroscopy and quantum chemistry. The authors freely admit that in molecular resonances which live 10^{-14} sec or less, there is perhaps a quantitative danger in drawing potential curves which depend on strict adherence to the Born-Oppenheimer approximation. For such short lifetimes it is dangerous to talk about potential curves, vibrational levels, etc. On the other hand, as a first approximation in quantitative calculations (as shown by Herzenberg et al.), and in qualitative explanations and predictions of experiment as shown above and in TNG, the usefullness of the quasi-stationary approach and chemical intuitive ideas cannot be denied.

Calculations

Calculations were done on CE1, CE2, and SP resonances. For CE1, the quasivariation method of TW is adequate, as evidenced by the results published in TW. However, to calculate the CE2 and SP resonances, the stabilization method must be used. Hence a basis set for use in the stabilization method must be constructed which is physically reasonable and insures convergence (stabilization) with as few functions as possible.

The calculations were done with the diatomic molecule program of Harris (1960) and Taylor and Harris (1963, series), modified to include the quasivariation and stabilization methods. In this program, trial functions are composed of linear combinations of products of one electron orbitals, so the one electron orbital basis is what is sought for the stabilization method, as used here.

For a homonuclear diatomic molecule, suitable molecular orbitals are defined as

$$\emptyset_r(\delta,\alpha;nm\nu p) = \exp[-\delta\xi+i\nu\varphi]\ \xi^n[(\xi^2-1)(1-\eta^2)]^{|\nu|/2}\cdot \eta^m\Big\{\exp[-\alpha\eta] + (-1)^k \exp[\alpha\,\eta]\Big\} \tag{1}$$

where ξ, η, φ are the prolate spheroidal coordinates; δ, α are non-linear variable parameters; n, m are integer exponents; ν is the

azimuthal quantum number; p defines <u>gerade</u> or <u>ungerade</u> symmetry of the orbital; r indexes the root of the chosen symmetry which most corresponds to the particular orbital ϕ_r. The exponent k is used to produce the <u>g</u> or <u>u</u> symmetry defined by p through the relation $k = m + p + |\nu|$ where p is even for <u>g</u> and odd for <u>u</u>. A complete discussion may be found in the theses of either of the authors.

A more compact notation

$$r\lambda_p = \phi_r(\delta,\alpha;nm\nu p) \tag{2}$$

is now possible, and will be used in the following discussion. As example,

$1\,\sigma_g = \phi_1(\delta,\alpha;0000)$, $1\,\sigma_u = \phi_1(\delta,\alpha;0001)$, and $1\,\pi_u = \phi_1(\delta,\alpha;00{\pm}11)$.

Note that (1) is a highly flexible function with two variable non-linear parameters.

One possible choice of basis would be a set of orbitals as near H_2^+ orbitals as possible, and the functions (1) can be selected to give an excellent representation of these orbitals. For example, at R = 2.0 au (1 au = .52917 Å), the equilibrium separation for the ground state of H_2^+, a $1\,\sigma_g$ orbital of the type (1) gives an energy only 0.00002 Hartree above the exact energy as determined by Bates, Ledsham, and Stewart (1953). A basis of this type would be ideal for electron-H_2^+ scattering calculations, but for the target H_2 and calculations on CE resonances a slight modification causes faster stabilization. The basis was actually chosen by the following steps:

1. For a particular internuclear separation R, the best $1\,\sigma_g$ H_2^+ orbital is found. As is known, this gives an

excellent representation of the innermost orbital of the excited H_2 states which is desirable since core-excited resonances are in the field of the excited H_2 states are to be studied.

2. A $1\sigma_g'$ orbital is then added and holding $1\sigma_g$ fixed, is minimized to make the best one term ground state of H_2. Due to the fixed H_2^+ orbital, this one configuration H_2 result is not the best that could be achieved with the diatomic program.

3. $1\sigma_u$ and $1\pi_u$ orbitals are found by minimization in the field of the $1\sigma_g$ H_2^+ orbital to make the best one term ${}^{3,1}\Sigma_u^+$, and ${}^{3,1}\pi_u$ states of H_2.

4. Higher orbitals $2\sigma_g, 3\sigma_g \cdots$; $2\sigma_u$, $3\sigma_u \cdots$; and $2\pi_u$, $3\pi_u \cdots$ are constructed by minimization of higher roots of the secular equation with the trial function

$$C_1 \, 1\sigma_g \, 1\lambda_p + \sum_{n=2}^{r} C_n \, 1\sigma_g \, n\lambda_p$$

holding the $1,2,\ldots r-1$ orbitals fixed.

The sets of orbitals of σ_g, σ_u, π_u symmetry for various values of R which were used in the CE calculations are listed in Tables 4-6.

Products of three of these orbitals are used as a basis for the H_2^- calculations, and in the major configurations representing the CE1 resonances the parameters of the outermost orbital were also varied to minimize the energies of the roots which were being stabilized. As all resonance energies (even those obtained by the quasivariation method) were checked for stabilization, this introduced no difficulties.

TABLE 4

σ_g BASIS ORBITALS

R	No.-nmv $1\sigma_g$-000 δ	$1\sigma_g$-000 α	$1\sigma_g{}'$-000 δ	$1\sigma_g{}'$-000 α	$2\sigma_g$-100 δ	$2\sigma_g$-100 α	$3\sigma_g$-300 δ	$3\sigma_g$-300 α	$4\sigma_g$-220 δ	$4\sigma_g$-220 α	$5\sigma_g$-120 δ	$5\sigma_g$-120 α	$6\sigma_g$-400 δ	$6\sigma_g$-400 α
1.05	.828891	.524856	.526042	.58879	.26193	.36369	.2112	0	.19393	0	.28326	0	.34924	0
1.1	.8593	.5465	.538	.611	.270	.379	.21884	0	.201	0	.29385	0	.36273	0
1.2	.920154	.589154	.581989	.655448	.29077	.408248	.23444	0	.21529	0	.31445	0	.38769	0
1.3	.978761	.632081	.616848	.698727	.30929	.37115	.24937	0	.22900	0	.33448	0	.41238	0
1.4	1.035916	.673943	.651460	.738934	.327351	.39282	.26393	0	.24237	0	.35401	0	.43646	0
1.5	1.091746	.715231	.686123	.781250	.34499	.41399	.27816	0	.25544	0	.37309	0	.45999	0
1.65	1.173099	.776848	.738635	.834097	.37070	.44480	.29888	0	.27447	0	.40090	0	.49426	0
1.8	1.252035	.837942	.783891	.900291	.39564	.47477	.31899	0	.29294	0	.42787	0	.52752	0
1.95	1.328873	.898702	.870353	1.067471	.41995	.52275	.33857	0	.31092	0	.95413	0	.55990	0
2.1	1.403905	.959319	.881643	1.00884	.44363	.53236	.35769	0	.32847	0	.47977	0	.59151	0
2.25	1.477368	1.019904	.924581	1.058824	.46685	.56022	.37640	0	.34566	0	.50488	0	.62246	0
2.4	1.549471	1.080594	.969630	1.113074	.48964	.58757	.39477	0	.36253	0	.54498	0	.65284	0
2.7	1.690336	1.202832	1.063269	1.21261	.53413	.64096	.43066	0	.39549	0	.57766	0	.71219	0
3.0	1.82778	1.326833	1.152866	1.307184	.57758	.69310	.46568	0	.42765	0	.62463	0	.77010	0

TABLE 5

σ_u BASIS ORBITALS

R	No.– nmν $1\sigma_u$-000 δ, α	$2\sigma_u$-010 δ, α	$3\sigma_u$-210 $\delta(\alpha=0)$	$4\sigma_u$-310 $\delta(\alpha=0)$	$5\sigma_u$-330 $\delta(\alpha=0)$	$6\sigma_u$-430 $\delta(\alpha=0)$*
1.05	.21729, .58879	.25995,.32588	.180	.129	.110	.06042
1.1	.23619, .62400	.27103,.35050	.189	.139	.111	.06092
1.2	.27958, .41937	.29978,.24054	.205	.153	.111	.06241
1.3	.33152, .58000	.29499,.34278	.222	.166	.112	.06389
1.4	.38369, .57554	.32389,.34177	.238	.185	.114	.06537
1.5	.42942, .64413	.34634,.38552	.258	.196	.116	.06320
1.65	.51134, .76701	.37185,.46725	.283	.214	.117	.06320
1.8	.60518, .87655	.39148,.54299	.313	.236	.118	.060014
1.95	.68580, .94750	.40800,.59700	.337	.258	.119	.060022
2.1	.79160,1.02830	.43431,.64647	.365	.277	.120	.063204
2.25	.88569,1.10406	.45595,.68393	.390	.300	.121	.063200
2.4	.97944,1.17610	.47770,.71655	.414	.327	.122	.063198
2.7	1.16486,1.33033	.52035,.78053	.462	.366	.123	.063167
3.0	1.34665,1.47984	.58694,.85341	.507	.404	.126	.062900

*as minimized in quasivariation method.

TABLE 6

π_u BASIS ORBITALS[a]

R	$1\pi_u$-001[b]	No.– nmν[b] $1\pi_u{}'$-001	$2\pi_u$-201	$3\pi_u$-121[c]
	δ α	δ α	δ(α=0)	δ(α=0)
1.05	.29985,.26207	.24643,.25342	.39992	.030842
1.2	.33999,.29611	.27877,.28377	.45418	.030945
1.3	.36774,.31632	.29700,.30400	.48924	.030601
1.4	.39577,.34203	.31723,.32423	.52305	.030586
1.5	.42356,.36445	.33737,.34642	.55802	.030600
1.65	.46481,.39771	.36822,.37589	.60816	.030610
1.8	.50548,.43069	.39871,.40923	.65713	.030604
1.95	.54556,.46347	.42907,.43554	.70496	.032944
2.1	.58508,.49599	.45885,.46585	.75164	.03049[d]
2.25	.62398,.52846	.48920,.49619	.79724	.086289
2.4	.66240,.56064	.51954,.52654	.84183	.08868
2.7	.73775,.62522	.58014,.58327	.92783	.089045
3.0	.81159,.68984	.64243,.64518	1.01001	.088043

a - π_g orbitals are made by taking the g counterpart of these.

b - The orbital $1\pi_u$ was used to form the $c\,^3\Pi_u$ state of H_2, and the $1\pi_u{}'$ to form the $C\,^1\Pi_u$ state.

c - As minimized in quasivariation method.

d - nmν changed to 42-1 for all R values below here.

No parameters were varied in CE2 or SP calculations once the basis was obtained, as this could lead to disastrous results.

The spin eigenfunctions used were the two three-electron doublets

$$\frac{1}{\sqrt{6}}(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)$$

and (2)

$$\frac{1}{\sqrt{2}}(\alpha\beta\alpha - \beta\alpha\alpha)$$

which can be seen to be $C_1\ \alpha\alpha\cdot\beta + C_2(\alpha\beta + \beta\alpha)\cdot\alpha$ and $C_1(\alpha\beta - \beta\alpha)\cdot\alpha$ respectively, or therefore one doublet composed of the two electron triplet plus an electron, and one composed of the singlet plus an electron. In the complete open shell treatment (different orbitals for different electrons), both spin doublets are used, and the coefficients corresponding to a particular combination of a spatial configuration (product of three one-electron molecular orbitals) and spin doublet gives an indication of the two electron target state to which the third electron became attached.

The first problem considered was the attempt to improve the results of TW, and to see if two CE1 resonances could be found, rather than the one reported in TW.

Hence the first calculational step was to do a calculation in which ${}^{3,1}\Pi_u \cdot n\pi_u$ and ${}^{3,1}\Sigma_g \cdot n\sigma_g$ were mixed and the ground state of H_2 projected out in accordance with the quasivariation method as discussed in TW. The singlet and triplet were automatically mixed by the use of both doublets, so that only two spatial configurations were necessary.

The result was that even though the two electron spatial configurations of the two triplet states were quite close in energy, the three electron states did not mix to six orders of magnitude, and the singlet and triplet parent spin doublets also did not mix. The two-electron Π states have considerably more electron affinity than the Σ states, and both CE1 resonances can thus be formed from ${}^{3,1}\Pi_u$ plus an electron, with the ${}^{3,1}\Sigma_g$ plus an electron yielding CE2 resonances.

The results presented are actually two-configuration results, because the parent target states ${}^3\Pi_u$ and ${}^1\Pi_u$ were determined with two configurations, $(C_1 1\sigma_g 1\pi_u + C_2 1\sigma_u 1\pi_g)$. In the singlet Π state, the orbitals $1\pi_u'$, $1\pi_g'$ of Table 6 were used instead of $1\pi_u, 1\pi_g$. C_1 was $\sim .99$ and $C_2 \sim .02$ at all internuclear distances. For the three electron calculation, the $3\pi_u$ orbital was added, and its non-linear parameters varied to minimize the energy. The linear coefficients were unchanged.[11]

The agreement with experiment demonstrates the efficacy of the one-electron model (product of one-electron functions with small number of configurations). At several R values, additional configurations were added, including higher π_u orbitals, but no additional

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[11] Actually, in a two spatial configuration three electron doublet calculation there are four roots, and four linear coefficients. Since the roots corresponding to the triplet and singlet spin parents do not mix, equivalent results are obtained by using only the doublet $1/\sqrt{6}\,(2\alpha\alpha\beta-\alpha\beta\alpha-\beta\alpha\alpha)$ with the lower CE1 resonance, and the doublet $1/\sqrt{2}\,(\alpha\beta\alpha-\beta\alpha\alpha)$ with the upper. Then the linear coefficients are unchanged from the two electron calculations. This provides a useful simplification if the wave functions are to be used for further calculations, such as widths, etc.

binding to the ${}^{3,1}\Pi_u$ states was obtained. The energy did improve, but only to the extent that the energy of the two-electron states themselves improved. In the interest of computer time, and since the necessary quantitative information for comparison to experiment has been obtained, the two configuration results are considered adequate.

Stabilization was checked by adding configurations of the type $e \cdot H_2(X^1\Sigma_g^+)\ {}^2\Sigma_g^+$, i.e. $\left\{ C_1\sigma_g\sigma_g{}' + C_2\sigma_u\sigma_u{}' + C_2\pi_u\pi_u{}' \right\} \cdot n\sigma_g$, $n = 2,3$, etc. The roots corresponding to the CE1 resonances were immediately stable to six figures, the matrix elements between the CE1 resonances and the stabilizing configurations were completely negligible (10^{-8} or less) and the corresponding coefficients in the eigenvector matrix therefore were also negligible. Addition of more $n\sigma_g$ orbitals only served to slightly lower the lowest root to an energy nearer the correct energy of the ground state of H_2, and inserted unstable roots between the lowest root and the root corresponding to the CE1 resonance (plus meaningless roots above the expected range of the CE2 resonances).

The next step was a quasivariation calculation of the resonance corresponding to $e \cdot {}^3\Sigma_u^+$ for comparison to the dissociative attachment experiment.

At large R values, no difficulties were observed, but as R was decreased into the Franck-Condon region, the amount of binding for the third electron also decreased. Somewhere between 1.4 and 1.3 au (R) the binding for the third electron became negligible (0.07 eV or less), and as R was decreased further, the potential curves for the CE1 ${}^2\Sigma_g^+$ resonances and the ${}^3\Sigma_u^+$ repulsive state of H_2 were coincident for all

practical purposes. This result is consistent with the model of crossing to form a CE2 resonance in the Franck-Condon region. The stabilization method was applied next. When the roots for R greater than or equal 1.5 au were checked, no change was observed, and the mixing of the stable resonance configurations and the stabilizing configurations was negligible.

However, for smaller R values, the mixing is not negligible, and the roots corresponding mainly to the resonance configurations began to move to higher energy values. Stabilizing configurations of the type $^1\Sigma_g^+ \cdot n\sigma_g$ were used, for n from two to seven. The roots corresponding to the resonance usually stabilized once the three stabilizing configurations $^1\Sigma_g^+ \cdot \left\{C_1 2\sigma_g + C_2 3\sigma_g + C_3 4\sigma_g\right\}$ had been added, however three additional configurations were added at each R as a precautionary check.

The final result obtained was that for the smallest R considered, 1.05 au, the $^2\Sigma_g^+$ resonances was 0.2 eV above the $^3\Sigma_u^+$ state of H_2, and that the resonance changed from CE1 to CE2 between 1.4 and 1.5 au.

In these calculations, simple products of one-electron orbitals were again used, with the $^3\Sigma_u^+$ of $1\sigma_g 1\sigma_u$ and $^2\Sigma_g^+$ of $1\sigma_g 1\sigma_u 6\sigma_u$ from Tables 4-6. For R $\geq$ 1.5 au only the one-configuration result and considerably easier to apply for any further calculations. For R < 1.5 the CE2 resonance mixes with the stabilizing configurations, so the entire eigenvector is presented for the stable CE2 root at each R in Table 7. The numbers to the left of the table indicate the space-spin configuration, with eleven spatial configurations and the two spin

TABLE 7

EIGENVECTORS FOR STABILIZATION OF $^2\Sigma_g$ CE2 ROOTS

Basis Orbitals for Configurations

Configuration	Orbitals
1	$1\sigma_g 1\sigma_u 6\sigma_u$
2	$1\sigma_g 1\sigma_u 5\sigma_u$
3	$1\sigma_g 1\sigma_u 4\sigma_u$
4	$1\sigma_g 1\sigma_u 3\sigma_u$
5	$1\sigma_g 2\sigma_u 6\sigma_u$
6	$1\sigma_g 2\sigma_u 5\sigma_u$
7	$1\sigma_g' 1\sigma_u 6\sigma_u$
8	$1\sigma_g' 1\sigma_u 5\sigma_u$
9	$1\sigma_g 1\sigma_g' 2\sigma_g$
10	$1\sigma_g 1\sigma_g' 3\sigma_g$
11	$1\sigma_g 1\sigma_g' 6\sigma_g$

TABLE 7

EIGENVECTORS FOR STABILIZATION OF $^{2}\Sigma_{g}$ CE2 ROOTS

NO.	R = 1.05	R = 1.1	R = 1.2	R = 1.3	R = 1.4
	-0.6333982E 00	-0.6623221E 00	-0.7024906E 00	-0.7379915E 00	-0.7721574E 00
1	0.1626913E-01	-0.1799859E-01	0.8579724E-01	0.1817709E-01	-0.5638126E-02
2	-0.2056712E-02	-0.3541176E-04	-0.3222728E-03	0.2535066E-03	0.8700729E-04
3	0.1891520E 00	0.1512853E 01	0.3306830E 00	0.2490221E 00	0.8967400E 00
4	-0.9952046E-01	0.1312127E-01	-0.1268227E-01	-0.5480240E-02	-0.1467705E-02
5	0.8521528E 00	-0.3879741E 00	0.7026666E 00	0.7172456E 00	-0.1789682E 00
6	0.1507833E-01	-0.1350495E-01	0.1179436E-01	0.1107371E-01	0.1113198E-02
7	-0.8875945E-01	0.1191307E 00	-0.9267284E-01	-0.9645079E-01	0.7124905E-01
8	-0.1821999E-01	0.4141217E-02	-0.1494963E-01	-0.1321234E-01	-0.1930247E-02
9	-0.8573794E-03	0.1171185E-01	0.3093459E-02	-0.5640836E-03	0.8456775E-02
10	-0.1099810E-02	0.5381343E-04	-0.3068288E-03	0.2253430E-04	0.4016789E-04
11	0.6099185E-01	-0.4095204E-01	0.7695860E-01	-0.6434724E-02	-0.4359872E-01
12	-0.7874269E-01	0.1858734E-02	-0.8367922E-02	-0.1632179E-02	-0.1277026E-02
13	-0.4382460E-02	0.2753270E-01	-0.1431650E-01	-0.2129001E-01	0.7134695E-02
14	-0.9068978E-03	-0.3336346E-03	-0.1253954E-03	-0.5909892E-04	-0.5025168E-04
15	0.9478928E-01	0.8696452E-01	0.1297499E 00	0.1563071E 00	0.1714288E 00
16	0.2301585E-02	0.7572825E-03	0.4641221E-03	0.1575546E-03	0.1048079E-03
17	0.8518396E-03	0.4349481E-02	0.6908290E-03	0.5431062E-03	0.4017436E-02
18	0.2244960E-02	0.5479784E-02	0.2209623E-02	0.2193951E-02	0.6280439E-02
19	0.1301200E-01	0.6138788E-02	0.1277370E-01	0.1262201E-01	0.7162635E-02
20	0.4948678E-03	0.1796536E-02	0.4397392E-03	0.4378694E-03	0.2232344E-02
21	-0.2010764E-02	-0.3648769E-02	-0.1733061E-02	-0.1460910E-02	-0.3894991E-02
22	-0.1559114E-02	-0.5276457E-02	-0.1566271E-02	-0.1584944E-02	-0.6304872E-02

doublets. The odd indices correspond to the combination of a particular spatial configuration and the triplet spin parent $1/\sqrt{6}$ $(2\alpha\alpha\beta-\alpha\beta\alpha-\beta\alpha\alpha)$, while the even indices correspond to the combinations with the singlet spin parent $1/\sqrt{2}$ $(\alpha\beta\alpha-\beta\alpha\alpha)$. The orbitals from Tables 4-6 which make up the eleven configurations are denoted in Table 7. The eigenvectors for the largest, eleven configuration, stabilizing calculation are given rather than a smaller calculation with the same stable root in order to show the relative mixing of the different stabilizing configurations.

These results, and the results of the upper CE1 calculations are presented graphically in Fig. 1. The solid lines correspond to resonances of H_2^-, and the dashed lines to one-electron model calculations of the parent H_2 states. Note that as a result of using a $1\sigma_g H_2^+$ orbital as one of the major elements of the basis set in order to get rapid stabilization of the core-excited resonances, the single configuration calculations for the excited H_2 states are quite good. The CE1 to CE2 crossing point is determined relative to the $^3\Sigma_u^+$ H_2 curve calculated with the same basis.

It is also to be noted that the $^2\Sigma_g^+$ repulsive curve and the $^2\Sigma_g^+$ curve of $e \cdot {}^3\Pi_u$ do become nearly tangent at small R values. In fact, from the slopes in Fig. 2, it is possible that they may intersect. Therefore, at two small R values, 1.05 and 1.2 au, the $\sigma_g\sigma_u\sigma_u'$ and $\sigma_g\pi_u\pi_u'$ configurations were mixed again as a check. The off-diagonal elements were $\sim 10^{-8}$ smaller than the diagonal elements in both cases, indicating that whether the non-crossing rule holds or not, the mixing of the two states is so small that if the nuclei possess any kinetic

energy at all, they will follow the diabatic curve rather than the adiabatic, as discussed in the preceding section.

For the stabilization of the two SP resonances of symmetry $^2\Sigma_u^+$ an entirely different procedure was used. Since the SP resonances are physically considered to be a σ_u electron in the field of the slightly polarized ground state, the first step was a full three-configuration variation treatment of the ground state of H_2. The $\sigma_g 1s$ and $\sigma_g 1s'$ are thus not the same as those listed in Table 4, but those which make the best ground state H_2 one term calculation. $\sigma_u^c 1s$ and $\sigma_u^c 1s'$ were chosen as were π_u^c and $\pi_u^{c\prime}$ as correlating orbitals which minimized the ground state energy. This had to be done at each R point. In general, the orbitals with superscripts c are much more concentrated about the nuclei than the orbitals of Tables 4-6.

The first three-electron wave function was $\left\{C_1\sigma_g 1s\sigma_g 1s' + C_2\sigma_u^c 1s\sigma_u^c 1s' + C_3\pi_u^c 2p_{+1}\pi_u^c 2p'_{-1}\right\} \times \left\{\sigma_u^c 1s + \sigma_u^c 1s'\right\}$ and the roots obtained with this calculation were checked for stabilization by adding the σ_u orbitals from Table 5 one at a time to the H_2 ground state function in the first bracket. The trial function above mixed strongly with the first three of these stabilizing configurations, and the roots only began to settle down after the fourth excited σ_u orbital had been added.

This was a very extensive calculation involving a maximum of twelve one-electron orbitals and as many as twenty-one spatial configurations, which with the two spin doublets made a 42×42 secular equation. For this reason, only the energies and qualitative features of the wave functions have been presented. The parameters of all the

orbitals, the eigenvectors, etc. will be furnished upon request.

As in the CE2 cases, addition of stabilizing configurations tended to drive the root corresponding to the SP resonance configuration up, inserting spurious and unstable roots between it and the ground state and improving the ground state root. In contrast, CE1 resonances calculated by the quasivariation method, when stabilizing configurations were added, tended to have their energies slightly lowered, if any energy change occurred at all.

It is interesting to note that another root in the ${}^2\Sigma_u^+$ sequence became approximately stable, at energies about 1.5 - 2.0 eV above the region of the four states ${}^{3,1}\Pi_u$ and ${}^{3,1}\Sigma_g^+$ discussed previously. This probably corresponds to a poor calculation of the ${}^2\Sigma_u^+$ $(\sigma_u \cdot E\,{}^1\Sigma_g^+)$ mentioned above as a possible core-excited resonance. The singlet spin parent was definitely more important in the configuration, so it is also possible that the root could correspond to $e \cdot B\,{}^1\Sigma_u^+$, however this is felt to be less likely, since the stabilizing configurations tend to push the root up, not down. Further study is necessary to resolve this point, since no configurations other than ${}^2\Sigma_u(X\,{}^1\Sigma_g^+) \cdot n\sigma_u$ were included in the trial function, and these cannot be expected to give a good calculation for a CE state, even if a stable root should occur. At present, there is no way of knowing whether the upper root would even remain stabilized upon addition of core-excited configurations, as it did not seem to stabilize as rapidly as the SP root. The semistable roots are given in column (f) of Table 3, and the parentheses are used to indicate that they are not considered final or completely

stabilized, but do indicate the possible presence of a CE type resonance near that energy region.

Finally, it should be mentioned that calculations of resonance energies, particularly by the quasivariation method, are fraught with unforeseen and hidden difficulties not encountered in stationary state calculations. First, in every resonance calculated, if the energy was plotted as a function of the "screening parameter" δ of the outermost added orbital, pseudo-minima were encountered, a situation which had not occurred in the case of stationary state calculations with the diatomic molecule program used here. This is probably because variation of δ shifts the maximum electron density of the orbital so that it coincides with the maximum density of higher orbitals, even though the orbital exponents n and m are fixed and do not represent the nodal properties of the higher orbital properly. Each coincidence of electron density maxima would then produce a pseudo-minimum. An example of this is the quasivariation calculation of the $e \cdot {}^3\Pi_u$ resonance. At R = 3.0 au, essentially the same energy can be obtained with $\phi_3(.03056,.0;12\text{-}11)$ or $\phi_3(.0632,0;42\text{-}11)$ and fixed $\phi_1 = 1\sigma_g$ and $\phi_2 = 1\pi_u$. Both ϕ_3 orbitals exhibit false minima for larger δ values.

The second difficulty is with convergence of the two-electron integrals $(ij|1/r|k\ell)$ when very small δ values are used, particularly in the higher orbitals. Within the limitations set by the program, this problem is purely numerical, caused by the loss of significant figures upon subtraction of large numbers and exponent overflow, underflow and wraparound, and can be surmounted by the use of scaling and/or double precision arithmetic.

Third, there is the amount of physical and chemical intuition required to obtain good results. A poor guess of the major resonance configurations, or a poor trial function for them, may either greatly increase the amount of work necessary to get agreement with experiment, or yield completely meaningless results. The ability to calculate widths and energy shifts would greatly aid in the problem.

The consequence of these difficulties is that each resonance calculation must be approached as a completely separate problem requiring special, individual handling. There can be no doubt of the fact that the quasivariation and stabilization methods work, as the agreement with experiment reported here shows, but for these and any other calculations of resonant states, extreme caution is necessary. With a well determined basis set, and based on our experience with both methods the stabilization method appears to be preferable for reasons of both flexibility and safety.

The calculations were performed on the Honeywell 800 computer of the University of Southern California Computer Science Laboratory, and the LBM 7094/7044 DCOS equipment of the Jet Propulsion Laboratory. The authors would like to express their appreciation to both institutions for making available the large amounts of computer time which were necessary for these calculations.

CHAPTER IV

SUMMARY

Quasi-stationary methods of calculating the energy of core-excited and single particle resonances and autoionizing states of atoms and molecules are presented both from an intuitive, physical approach and from a formal, rigorous standpoint.

The methods are applied to resonant states of H_2^-, and in the process, a general computer program for calculating the energies and wave functions of diatomic molecules which incorporates both the normal variation method of quantum chemistry for bound states and quasi-stationary methods for resonances has been developed.

The results of the H_2^- calculations are compared to electron scattering experiments.

The diatomic molecule program developed is a modernization of previous methods including several new options, and extended so that calculations can be done for up to twenty electrons. It is fully discussed in a set of Appendices, and a sample calculation on NO^+ is presented as an illustration of the applicability of the program to calculations on large diatomic systems.

APPENDIX I. MATHEMATICAL DETAILS

Wave Function and Coordinate System

The diatomic molecule program discussed in these appendices is a generalized program for calculating the energy of a diatomic molecule within the Born-Oppenheimer approximation, using the variation method with optimization of both linear and non-linear parameters to improve the energy. The mathematical procedures used are an extension and generalization of the programs of Harris (1960), and Taylor and Harris (1963, etc.), and extensive use will be made of these references. The inclusion of the full mathematical treatment, rather than only the outline of its departures from the above methods, is for the purpose of completeness, so that these appendices will contain all the information necessary to understand and to use the diatomic program.

The total wave function is composed of linear combinations of products of one-electron molecular orbitals. These orbitals, ϕ_i, are expressed in prolate spheroidal coordinates, therefore the discussion will begin with the coordinate system and definition of the ϕ_i, and proceed stepwise to the definition of the total wave function.

The prolate spheroidal coordinate system is based on two foci, A and B, where the two nuclei are located. The foci are separated by the internuclear distance R. The coordinates of a point P_i are

(Fig. 8)

$$\xi_i = \left(r_{a_i} + r_{b_i}\right)\Big/R$$

$$\eta_i = \left(r_{a_i} - r_{b_i}\right)\Big/R \qquad (1)$$

φ_i = azimuthal angle about the internuclear axis.

The quantity ρ_i, the distance of P_i from the internuclear axis, is also useful, and is expressed as

$$\rho_i = \frac{1}{2} R \left[(\xi^2 - 1)(1 - \eta^2)\right]^{\frac{1}{2}} . \qquad (2)$$

The volume element and some differential forms in this system are

$$d\vec{r} = \frac{1}{8} R^3 \; (\xi^2 - \eta^2) \; d\xi d\eta d\varphi \qquad (3)$$

$$\nabla^2 f = \frac{4}{R^2(\xi^2-\eta^2)} \left[\frac{\partial}{\partial\xi}\left\{(\xi^2 - 1)\frac{\partial f}{\partial\xi}\right\} + \frac{\partial}{\partial\eta}\left\{(1 - \eta^2)\frac{\partial f}{\partial\eta}\right\} + \frac{(\xi^2-\eta^2)\dfrac{\partial^2 f}{\partial\varphi^2}}{(\xi^2-1)(1-\eta^2)}\right] \qquad (4)$$

$$\nabla f \cdot \nabla g = \frac{4}{R^2(\xi^2-\eta^2)} \left[(\xi^2 - 1)\frac{\partial f \partial g}{\partial\xi d\xi} + (1 - \eta^2)\frac{\partial f \partial g}{\partial\eta\partial\eta} + \frac{(\xi^2-\eta^2)}{(\xi^2-1)(1-\eta^2)}\frac{\partial f}{\partial\varphi}\frac{\partial g}{\partial\varphi}\right] \qquad (5)$$

with the limits $1 \leq \xi \leq \infty$, $-1 \leq \eta \leq 1$, $0 \leq \varphi \leq 2\pi$.

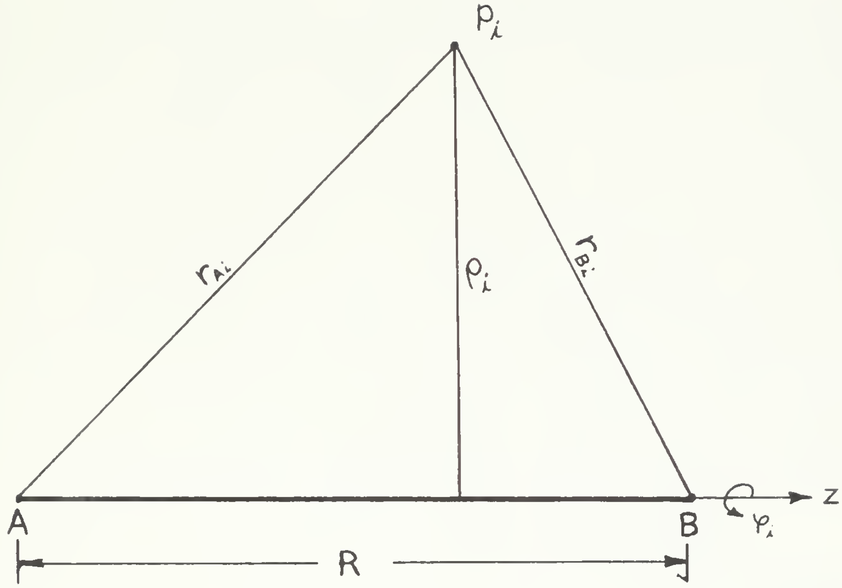

FIGURE 8

PROLATE SPHEROIDAL COORDINATE SYSTEM

The one electron spatial function $\emptyset_i$ is chosen in terms of these coordinates as

$$\emptyset_i(\vec{r}_j) = \exp\left[-\delta_i\xi_j - \alpha_i\eta_j + i\nu_i\varphi_j\right]\cdot \xi_j^{n_i}\eta_j^{m_i}\cdot(2\rho_i/R)^{|\nu_i|} \tag{6}$$

$$= \emptyset_i(\delta_i,\alpha_i;n_i m_i \nu_i)$$

where δ_i,α_i are adjustable non-linear parameters which will be determined by the variation method. The δ parameter is a measure of the extent of an ellipse of electron charge density about the two nuclei, and must be positive to assure that the function goes to zero as ξ goes to infinity. The ratio α/δ gives a measure of polarization along the internuclear axis since $\alpha = \delta$ centers the electronic charge on the nucleus at A and $\alpha = -\delta$ centers the charge on the nucleus at B. Intermediate α values allow improvement of the molecular orbital by allowing unsymmetrical, polarized charge distributions.

The exponents n_i, m_i, are restricted to positive integers or zero, and are used to form higher orbitals. Non-zero m_i introduce a node in the perpendicular bisector plane of the internuclear axis. ν_i is the azimuthal quantum number, and can assume any integer value, including zero. The $(2\rho_i/R)^{|\nu_i|}$ factor has been included to provide regularity on the internuclear axis, and because it provides simplifying cancellations in some of the integral expressions to be introduced later.

Atomic orbitals, in particular Slater type orbitals, can be expressed as linear combinations of the elliptical functions $\emptyset_i$ without considerable difficulty, although the number of terms necessary in

the combination goes up quite rapidly as n increases. For example

$$1s_a = \emptyset(\delta,\delta;000)\ ,\quad 1s_b = \emptyset(\delta,-\delta;000)$$

$$2s_a = \frac{1}{2} R \left[\emptyset(\delta,\delta;100) + \emptyset(\delta,\delta;010)\right] \tag{7}$$

$$2s_b = \frac{1}{2} R \left[\emptyset(\delta,-\delta;100) - \emptyset(\delta,-\delta;010)\right]\ .$$

The remainder of the series can be generated using the fact that from (1) one can express

$$r_a = \frac{1}{2} R(\xi + \eta)$$

$$r_b = \frac{1}{2} R(\xi - \eta) \tag{1'}$$

In the homonuclear case, the problem of obtaining gerade or ungerade symmetry of the electronic wave function also presents itself. There are two methods of accomplishing this. One is the passing of the total molecular wave function through the center of inversion, taking the proper linear combination of the function and its inverted counterpart. This method will be discussed later, after introduction of the total wave function. The other is to symmetrize the individual molecular orbitals $\emptyset_i$, actually defining them as σ_g, σ_u, π_u, etc.

The symmetrization of the molecular orbital $\emptyset_i$ is accomplished by inverting it, and taking $\emptyset \pm \vec{i}\emptyset$ with the plus sign for gerade and the minus sign for the ungerade case. The $\vec{i}$ represents the inversion operation, which is equivalent to a reflection in the perpendicular bisector plane of the internuclear axis (interchange of A and B), followed by a rotation of pi radians ($\varphi \rightarrow \varphi + \pi$).

Examination of the function $\emptyset$ (Eq. 6) shows that this inversion is accomplished by replacing η by $-\eta$ and φ by $\varphi + \pi$, and therefore

$$\emptyset_{g,u} = \left\{ \emptyset(\delta,\alpha;nm\nu) + (-1)^k \emptyset(\delta,-\alpha;nm\nu) \right\} \frac{\sqrt{2}}{2} \tag{8}$$

where $k = p + m + |\nu|$; p representing the parity g or u desired, with p even for g and odd for u.

Since only certain portions of the function are affected by this operation, it is convenient to rewrite the symmetrized orbitals as

$$\emptyset_i^{g,u}(\delta,\alpha;nm\nu) = e^{-\delta_i\xi}\, \xi^n (2\rho/R)^{|\nu|}\, e^{i\nu\varphi} \cdot \left\{ e^{-\alpha_i\eta} + (-1)^k e^{\alpha_i\eta} \right\} \eta^m \tag{6'}$$

to eliminate excessive computational labor in the actual calculation of the spatial matrix elements.

Now let us define a primitive function $\Phi_j(\vec{r})$

$$\Phi_j(\vec{r}) = \prod_{i=1}^{N} \emptyset_i(\vec{r}_i) \tag{9}$$

where N is the number of electrons in the system, $\vec{r}_i$ is the position vector of the i^{th} electron, $\vec{r}$ symbolizes collectively the coordinates of all N electrons. The index j will be used to denote a particular spatial configuration after configuration interaction has been introduced.

A single spatial configuration is the antisymmetrized primitive function. **Combining** it with a spin function θ, one obtains the expression for a single configuration

$$\psi_{j\mu}(\vec{r},\vec{\sigma}) = \mathcal{A}_n(\Phi_j \theta_\mu) \tag{10}$$

where θ_μ is the μ^{th} eigenfunction of S^2 and $\vec{\sigma}$ represents the spin coordinates. Usually in this program one spatial configuration is combined with several spin eigenfunctions comprising a complete spin basis, but depending on the number of closed shell electrons selected in the problem. A more limited spin basis may be used, or a specific spin eigenfunction may be selected which most corresponds to the physical situation. Once a specific problem has been selected (i.e., lowest lying $^3\Sigma$ state of the molecule AB), the number of spin eigenfunctions will be fixed, so for simplicity the word configuration will be used to refer to a spatial configuration, realizing that this spatial configuration may be combined with one or several spin functions.

Defining d as the number of spin functions chosen for a particular problem and m as the number of configurations, the total trial wave function for the ℓ^{th} state of the system becomes

$$\Psi_\ell(\vec{r},\vec{\sigma}) = \sum_{i=1}^{m} \sum_{\mu=1}^{d} C^\ell_{i\mu} \, \psi_{j\mu}(\vec{r},\vec{\sigma}) \tag{11}$$

where the $C^\ell_{i\mu}$ are the components of the ℓ^{th} column of the eigenvector matrix determined by diagonalization of the secular equation.

It is now possible to show the method of producing g or u symmetry by inversion of the entire molecule through the inversion center.

The linear combination

$$c_1\Psi + c_2\vec{i}\,\Psi \tag{12}$$

can be considered as a two configuration problem, and the total secular matrix will be

$$\begin{pmatrix} \langle \Psi^* \mathcal{H} \Psi \rangle & \langle \Psi^* \mathcal{H} i\Psi \rangle \\ \langle i\Psi^* \mathcal{H} \Psi \rangle & \langle i\Psi^* \mathcal{H} i\Psi \rangle \end{pmatrix} \tag{13}$$

which is a supermatrix of m dxd blocks, and is of the form

$$\begin{pmatrix} A & B \\ B^+ & A \end{pmatrix} \tag{14}$$

since the matrix is Hermitian and $\langle i\Psi^* \mathcal{H} i\Psi \rangle = \langle \Psi^+ \mathcal{H} \Psi \rangle$.

If this is diagonalized for the energy, both g and u solutions will be obtained due to the form of (12), but it is well known that a matrix of the structure (14) can be diagonalized by the unitary transformation

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} \tag{15}$$

and applying this to the supermatrix (13) we obtain the block diagonal matrix

$$\frac{1}{2} \begin{pmatrix} \langle [\Psi + i\Psi]^* \mathcal{H} \, [\Psi + i\Psi] \rangle & 0 \\ 0 & \langle [\Psi - i\Psi]^* \mathcal{H} \, [\Psi - i\Psi] \rangle \end{pmatrix} \tag{13'}$$

or, taking advantage of (14) again, its simplified equivalent

$$\langle \Psi^* \mathcal{H} \, (\Psi \pm i\Psi) \rangle \tag{16}$$

Thus we see that Eq. (16) is equivalent to actually taking $\Psi_{gu} = \sqrt{2}/2(\Psi \pm i\Psi)$, but the amount of labor for calculation of

(16) with the proper sign is only about 3/4 that of calculating and diagonalizing either the g or u block of (13').

The program itself calculates the blocks A and B and then takes the sum or difference as necessary to select the desired symmetry for the molecule.

In the case of Σ states, if pi orbitals are included, plus-minus symmetry must also be considered. This can be handled by replacing ν_i by $-\nu_i$ in each pi orbital in a second configuration and repeating the calculation, and a procedure completely analogous to the above for selecting g or u symmetry can be used to select only the plus or minus linear combinations. Also, one could define a $\phi_{\pm}$ by replacing the $\exp(i\nu\varphi)$ factor in ϕ by

$$\left[\exp(i\nu\varphi) \pm \exp(-i\nu\varphi)\right] \tag{17}$$

in the pi orbitals of a configuration.

Spin and Antisymmetry

In the original diatomic methods (Harris, 1960; Taylor and Harris, 1963), spin and antisymmetry were handled by the method of representation matrices presented by Kotani, et al. (1963). This is an elegant group-theoretical approach in which a complete set of spin eigenfunctions is used as a basis to construct irreducible representation matrices, suitably antisymmetrized, for the n^{th} order permutation group σ_n. The method is completely general, and is particularly adaptable to the case of non-orthonormal spatial orbitals in the complete open shell (different orbitals for different spins)

treatment of the diatomic program.

Unfortunately, the number of mathematical operations in the complete open-shell treatment increases astronomically for larger systems, due to the n! permutations in the group σ_n, and the dimension of each of the set of n! representation matrices. For modern computers, the practical limit appears to be between six and eight electrons. In order to study larger systems, some sort of approximations must be made just to reduce these numbers to something in the realm of manageability.

One possibility is the closing of some or all of the shells (double occupancy). This has the effect of reducing the dimension of the representation matrices to only the invariant part corresponding to the remaining unpaired electrons as is outlined in Kotani, and of reducing the number of permutations necessary, since double occupancy causes linear dependencies in the group σ_n. If there are r paired orbitals, the number of permutations is reduced to $n!/2^r$. As an interim measure, this is helpful, but as n continues to increase, even closing of all the shells fails to reduce the problem to one of manageable size. For example, $16!/2^8$ is still of the order 14!, and even though the representation matrices are of dimension 1×1, it is clear that some other approach is necessary.

Another alternative is to introduce spatial orthogonalities, and by knowledge of where these orthogonalities exist, eliminate those permutations which can make no contribution to the total secular equation. This procedure can be used independently of the shell-closing procedure, or they can be used in conjunction. In the

16 electron case mentioned above, by orthogonalizing ten inner shell orbitals in closed pairs, and leaving six open-shell electrons for bonding, the size of the problem is reduced to somewhere between the seven and eight electron complete open-shell problems. This is still rather large, but well within the capabilities of a modern large scientific computer.

Thus one of the aims of this research has been to revise the spin-antisymmetry routines of the older versions of the diatomic program to include options which allow a range between complete open-shell and complete closed shell spin treatments, using any orthogonalities which are introduced or exist naturally to reduce the problem.

Since the formal treatment is fully presented in Kotani (1963), the remainder of this section will be mainly concerned with the actual mechanics of applying the method with all the options as it is done in the edition of the diatomic program presented here. The notation used is chosen to be as consistent with both Kotani and Taylor-Harris as possible. Unless otherwise noted, arguments of functions have been suppressed, and the coordinate number is indicated by position (i.e., $\phi_3(\vec{r}_1)\ \phi_1(\vec{r}_2)\ \phi_2(\vec{r}_3) = \phi_3\phi_1\phi_2$).

Let the two eigenfunctions of the one-electron operator $\underline{s}_z$ be denoted as α and β, with eigenvalues 1/2 and -1/2, respectively. Then eigenfunctions of the many-electron operator $\underline{S}_z$ can be represented as simple products of α and β,

$$\Omega = \alpha\alpha \cdots \beta\alpha\beta \cdots \quad . \tag{18}$$

with eigenvalue M. In general, there are

$$n_{\Omega} = \binom{N}{\frac{1}{2} N + M} \tag{19}$$

linearly independent simple product functions Ω for a given M value in an N electron problem; and the desired relation

$$\sum_{M=-N/2}^{N/2} \binom{N}{\frac{1}{2} N + M} = 2^N \text{ holds.}$$

The Ω functions are not generally eigenfunctions of $\underline{S}^2$ which, like $\underline{S}_z$, commutes with the Hamiltonian, but a simultaneous eigenfunction of $\underline{S}^2$ and $\underline{S}_z$ can be expressed as

$$\theta^N_{S,M} = \sum_i c_i \Omega_i \tag{20}$$

There are $f^N_S = \binom{N}{1/2N + S} - \binom{N}{1/2N + S + 1}$ functions $\theta^N_{S,M,k}$ $k = 1,2,\cdots F^N_S$ for given eigenvalues $S(S+1)$ of $\underline{S}^2$ and M of $\underline{S}_z$. In the diatomic program, the coefficients in the above expansion of $\theta^N_{S,M,k}$ are those generated by the method of genealogical construction (Kotani, 1963) which uses the vector coupling formula and the functions α and β to produce

$$\theta^N_{S,M,k} = - \sqrt{\frac{S-M+1}{2S+2}}\ \theta^{N-1}_{S+\frac{1}{2},M-\frac{1}{2};k} \cdot \alpha \sqrt{\frac{S+M+1}{2S+2}}\ \theta^{N-1}_{S+\frac{1}{2},M+\frac{1}{2};k}\ \beta$$

$$k = 1,2,\cdots F^{N-1}_{S+\frac{1}{2}} \tag{21}$$

and

$$\theta^{N}_{S,M,k} = \sqrt{\frac{S+M}{2S}}\ \theta^{N-1}_{S-\frac{1}{2},M-\frac{1}{2};h}\cdot\alpha \quad \sqrt{\frac{S-M}{2S}}\ \theta^{N-1}_{S-\frac{1}{2},M+\frac{1}{2};h}\cdot\beta \qquad k = F^{N-1}_{S+\frac{1}{2}} + h$$

$$h = 1,2\cdots F^{N-1}_{S-\frac{1}{2}} \tag{21}$$

This is not a unique choice of $\theta^{N}_{S,M,k}$, but any other choice may be expressed as a unitary transformation of this set. Katsura (1963), has published a set of all $\theta^{N}_{S,M,k}$ up to six electrons, and Weltin (1966) has developed a rapid and efficient scheme for generating all $\theta^{N}_{S,M,k}$ which is limited only by available storage space in the computer.

For the case of d and m both equal to one (one configuration and one spin function), so that the total wave function is represented by Eq. (10). The matrix element of an operator $\underline{O}$, which acts only on spatial coordinates, is

$$\left\langle \mathcal{A}_n\,[\Phi_1\theta_1]\ |\underline{O}|\ \mathcal{A}_n\,[\Phi_1\theta_1]\right\rangle \tag{22}$$

and using the Hermitian property of the antisymmetrizer plus the relation $\mathcal{A}_n^{\ 2} = \sqrt{n!}\,\mathcal{A}_n = \sum_P (-1)^p\, P$, (22) becomes

$$\sum_P (-1)^p \left\langle \Phi_1\theta_1\ |\underline{O}|\ P\left[\Phi_1\theta_1\right]\right\rangle \tag{22'}$$

where p is the even or odd parity of the permutation P. Since $P = P_r P_\sigma$, Eq. (22') can be separated to obtain

$$\sum_P \langle\Phi(\vec{r})|\underline{O}|\Phi(P_r\vec{r})\rangle\ \langle\theta(\vec{\sigma})|(-1)^p\theta(P_\sigma\vec{\sigma})\rangle \tag{23}$$

where the $(-1)^p$ has been included in the spin integral for convenience. Calculation of the spin integrals yields a set of coefficients $U_\mu(P)$, so that the matrix element can be expressed as

$$\sum_P U_\mu(P)\langle\Phi|\underline{O}|P\Phi\rangle = \sum_P U_\mu(P)\ \underline{O}(P) \tag{24}$$

with the definitions

$$\begin{aligned} \underline{O}(P) &= \langle\Phi|\underline{O}|P\Phi\rangle \\ U_\mu(P) &= (-1)^p\ \langle\theta|P\theta\rangle \end{aligned} \tag{25}$$

where the permutation is on either the functions or the coordinates in both integrals.

Additional spin functions may be introduced in which case the set $U_\mu(P)$ becomes a matrix of dimension d, where d is the number of spin eigenfunctions in the basis. Thus for one configuration, the matrix element of the operator $\underline{O}$ becomes a dxd matrix of the form

$$\sum_P U(P)\ \underline{O}(P) \tag{26}$$

where

$$U(P) = \left[U_{\mu\nu}(P)\right] = (-1)^p \langle\theta_\mu|P\theta_\nu\rangle \tag{27}$$

The secular equation for the energy is then

$$\sum_P U(P)\ [\underline{H}(P) - E\underline{S}(P)] = 0 \tag{29}$$

If the complete set of spin eigenfunctions is included ($d = F_S^N$) the matrices U(P) become unitary, irreducible representations of the permutation group, and are exactly the U(P) defined in Kotani (1963) and the Taylor-Harris papers (1960, 1963, etc.).

When spatial configuration interaction is included, the definition of $\underline{O}(P)$ can be expanded to $\underline{O}_{jk}(P) = \langle \Phi_j | O | P\Phi_k \rangle$, and the total secular matrix (29) becomes an mxd matrix, composed of dxd blocks for each $H_{jk}(P)$, $S_{jk}(P)$; $j,k = 1,2,\cdots m$.

Given the sets $\theta^N_{S,M,k}$, it is now possible to generate the representation matrices $\underline{U}(P)$ systematically, thus completely separating the spin and space parts of the problem, since once generated, the $\underline{U}(P)$ are general for any problem with the same N,S, and M. From Eq. (27)

$$U_{\mu\nu}(P) = (-1)^p \left\langle \theta^N_{S,M,\mu} | P\theta^N_{S,N,\nu} \right\rangle \tag{27'}$$

and therefore for an arbitrary permutation P, the associated $\underline{U}(P)$ may be generated from a single rectangular matrix $\underline{C}$, which has n_Ω rows and d columns stemming from the expansion of $\theta^N_{S,M}$ in terms of the Ω_i (Eq. 20).

Thus the μ,ν elements

$$U_{\mu\nu}(P) = (-1)^p \left\langle \sum_{i=1}^{d} C_{i\mu}\Omega_i \;|P \sum_{j=1}^{d} C_{\nu j}\Omega_j \right\rangle$$

$$= (-1)^p \sum_{i=1}^{d} \sum_{j=1}^{d} C_{i\mu} \cdot C_{Pj\nu} \left\langle \Omega_i | \Omega_{Pj} \right\rangle$$

where $P\Omega_j = \Omega_{Pj}$, which is a member of the complete Ω set, and due to the orthogonality of the Ω

$$U_{\mu\nu}(P) = (-1)^p \sum_i \sum_j C_{i\mu}\, C_{Pj\nu}\, \delta_{i,Pj} \;.$$

This is repeated for all μ,ν; $1 \leq \mu \leq d$, $1 \leq \nu \leq d$ to make the full matrix. The α's and β's are easily represented in a digital computer

as 0's and 1's, making the operation $P\Omega_j$ and the checking of $\delta_{i,Pj}$ relatively simple.

For a truncated θ_k basis, depending on the functions which are omitted, certain rows in $\underline{C}$ may have only zero elements ($C_{i\mu} = 0$; $1 \leq \mu \leq d$). If so, those rows are omitted, and the multiplication by zero handled implicitly by the Kronecker δ function for computational convenience.

Since it is now possible to form the matrix $\underline{U}(P)$ for any arbitrary P, the next requirement is a method of generating all the permutations P of the group σ_n. Harris (1960) devised a simple algorithm for systematically generating all N! permutations of the full group, optimizing mathematical operations and scan time.

Consider the arbitrary permutation P. It is desired to generate the succeeding permutation Q in as few operations as possible and such that Q is not a repetition of some permutation generated prior to P.

Read the numbers in P from left to right until the first increase occurs (i.e., first number which is larger than the one to its left). The position of this number is called the pivot position. Interchange the number in the pivot position with the largest number to its left which is less than the number itself. Simply copy (leave unchanged) everything to the right of this position. Then arrange all numbers to the left of the pivot position in ascending order. The result is the permutation Q. If there was no increase, all permutations have been generated.

For example, consider P represented by $\underline{i}/1\ \underline{j}/2\ \underline{k}/3\ \underline{\ell}/4 \ldots s/n$, with $i > j < k > \ell$, and $i > k$. The pivot position is 3, occupied by k. By the inequalities, j is the largest number less than k, so j and k are interchanged and $\underline{\ell} \ldots . \underline{s}$ are left as they were. Then i is greater than k, so they are rearranged in ascending order, and the resulting Q representation is $\underline{k}/1\ \underline{i}/2\ \underline{j}/3\ \underline{\ell}/4 \ldots s/n$.

The parity is easily determined by inspection of the canonical number of the position immediately to the left of the pivot position, c_{piv-1}. If c_{piv-1} [Mod. 4] is less than two, the parity of Q is opposite to that of P, and if it is ≥ 2, the parity of Q is the same as that of P. In the example above $c_{P-1} = 2$, and 2[Mod. 4] = 2, therefore Q and P have the same parity.

Table 8 gives a full numerical illustration of the results of the above techniques for the case of a complete open-shell three electron doublet, with two spin functions $\theta^3_{\frac{1}{2},\frac{1}{2},1}$ and $\theta^3_{\frac{1}{2},\frac{1}{2},2}$, and six permutations in the order they are generated.

The above procedure is general for any number of θ functions, but if closed shells are introduced and the dimension of the θ set reduced concomitantly, the U(P) become linearly dependent. (The expression "closed shells" is to be interpreted as strict double occupancy.) It is still possible to generate all the N! permutations and U(P), but a much more favorable computational situation would occur if a way of generating only the linearly independent subset of P and U(P) could be determined.

TABLE 8

SPIN-PERMUTATION MATRICES FOR THE OPEN-SHELL THREE ELECTRON DOUBLET

$$\theta^{3}_{\frac{1}{2}\frac{1}{2}1} = \frac{1}{\sqrt{6}} (2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)$$

$$\theta^{3}_{\frac{1}{2}\frac{1}{2}2} = \frac{1}{\sqrt{2}} (\alpha\beta\alpha - \beta\alpha\alpha)$$

Eigenvector matrix $\underline{C}$

$\Omega \backslash \theta$	1	2
$\alpha\alpha\beta$	$2/\sqrt{6}$	0
$\alpha\beta\alpha$	$-1/\sqrt{6}$	$-1/\sqrt{2}$
$\beta\alpha\alpha$	$-1/\sqrt{6}$	$-1/\sqrt{2}$

P	p	U(P)
1 2 3	(+)	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
2 1 3	(-)	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$
1 3 2	(-)	$\frac{1}{2}\begin{pmatrix} 1 & -\sqrt{3} \\ -\sqrt{3} & -1 \end{pmatrix}$
3 1 2	(+)	$\frac{1}{2}\begin{pmatrix} 1 & -\sqrt{3} \\ \sqrt{3} & 1 \end{pmatrix}$
2 3 1	(+)	$\frac{1}{2}\begin{pmatrix} 1 & \sqrt{3} \\ -\sqrt{3} & 1 \end{pmatrix}$
3 2 1	(-)	$\frac{1}{2}\begin{pmatrix} 1 & \sqrt{3} \\ \sqrt{3} & -1 \end{pmatrix}$

For r closed shell pairs of electrons, the θ basis becomes

$$\theta^{N}_{S,M,k} = \theta^{N-2r}_{S,M,k} \; (\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)\cdots(\alpha\beta-\beta\alpha)\left(\frac{\sqrt{2}}{2}\right)^{r}$$

$$k = 1,2,\cdots f^{N-2r}_{S} \qquad (30)$$

and there are $N!/2^r$ linearly independent matrices and permutations in the subgroup of σ_N. The generation of the U(**P**) is the same as before, except using the reduced θ basis so the problem becomes one of generation of only the linearly independent subset of permutations.

The Harris algorithm can easily be adapted to this problem. If an auxiliary permutation vector R is introduced, such that the vector **P** contains the actual function (coordinate) numbers, and R contains a set of dummy indices in which the closed shells are represented by duplicated numbers, a linearly independent subset can be generated by doing the permutation-generating scan over R, performing the same operations on **P**, and using **P** to generate U(**P**) and $\underline{O}$(**P**).

For example, a six electron triplet might have the form

$$\frac{\sqrt{2}}{4}(\alpha\beta+\beta\alpha)(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)$$

and the corresponding initial **P** and R would be

$$\mathbf{P} - 1\ 2\ 3\ 4\ 5\ 6$$

$$R - 1\ 2\ 3\ 3\ 5\ 5\ .$$

As an even more complete example, consider the three electron doublet with one closed shell pair, whose spin eigenfunction is $\theta^3_{\frac{1}{2}\frac{1}{2}2}$, and whose **P** and U(**P**) can be represented by the $U_{2,2}$ elements of the six permutation matrices of Table 8. Here it is seen that of the set of six permutations, if electrons one and two are the same, 123-213, 132-231, and 312-321 are equivalent, and moreover, that the 2,2 elements of their matrices are also identical. Thus selection of three of the non-equivalent permutations with their respective matrices would

only have the effect of multiplying the total secular equation by a constant, in this case 1/2.

Setting the initial P and R as 123 and 113 respectively, the sequence of permutations becomes

$$
\begin{array}{llll}
P - 123(+) & 231(+) & 321(-) \\
R - 113(+) & 131(+) & 311(-)
\end{array}
$$

so we see that the search over R will produce $3!/2 = 3$ non-equivalent permutations and using P to generate U(P) and $\underline{O}$(P) will produce the desired secular equation.

The preceding techniques can be applied automatically by the present modification of the diatomic program. The case of orthogonal functions is slightly less easy to generalize, and thus requires some planning on the part of the user before proceeding to the computation stage. No modification of the program is necessary, only careful preparation of the input data cards.

A completely orthogonal spatial basis would have non-zero elements only in the case of pairwise interchanges and the identity permutation.

For any other case, one must consider the spatial orthogonalities and the coordinate operators. Clearly, the set of permutations used must include all possibilities of one or two electron operators contributing to the secular equation. Thus, any permutation of a configuration which produces no more than two zero factors in S(P) must be included, and conversely, any permutations which may be seen to include three or more overlap factors which are zero may be excluded.

In a many configuration calculation, the configuration with the minimum number of orthogonalities controls the exclusion of permutations.

This option has been included in the program by allowing the user to generate a set of permutations particular to his problem by hand and instruct the permutation generating routine of the program of the specific limitations placed upon it. The program will generate any additional permutations as required and produce the reduced set of U(P) delineated by the permutations.

As an example, see the NO^+ calculation reported elsewhere in this work (page 140 ff.) which was included specifically for the purpose of illustrating the use of this option.

A word of caution is necessary here. When a complete spin basis is used, and the full N! set of matrices U(P) is thus generated, the ordering of the one-electron spatial functions in each configuration is energetically immaterial, since re-ordering is a unitary transformation, and the eigenvalues will not be changed. However, the eigenvectors will reflect the re-ordering transformation, and they will be changed accordingly.

On the other hand, if a truncated spin basis is used, whether all N! U(P) are generated or not, the eigenvalues will be dependent on the order, and for best results, the spatial functions <u>must</u> be ordered to correspond physically to the ordering of the α and β in the spin functions.

If one takes advantage of the orthogonality options, obviously the functions must be ordered to correspond with the set of hand-

generated permutations, and the ordering must be preserved in all configurations of a multi-configuration problem.

Matrix Elements

To produce the secular equation (29), the spatial integrals H(P) and S(P) must be evaluated. From Eq. (25), these are recognized as

$$S_{j\kappa}(P) = \left(\Phi_j \middle| P\Phi_\kappa\right) \tag{31}$$

and

$$H_{j\kappa}(P) = \left(\Phi_j \middle| \mathcal{H} \middle| \Phi_\kappa\right) \tag{32}$$

where

$$\mathcal{H} = \frac{Z_A Z_B}{R} + \sum_{i=1}^{n} h_i + \sum_{i \leq j < i}^{n} \frac{1}{r_{ij}} \tag{33}$$

and

$$h_i = -\frac{1}{2}\nabla_i^2 - \frac{Z_A}{r_{iA}} - \frac{Z_B}{r_{iB}} \tag{33'}$$

Z_A and Z_B are the charges of nuclei A and B, separated by the distance R. The distances r_{xy} are the distances between particles x and y. Atomic units are used, with energies in Hartrees (1 au = 27.21 eV), and length in Bohrs (1 au = .52917 Å).

Since no term of $\mathcal{H}$ includes the coordinates of more than two electrons, H(P) is reducible to sums of products of one- and two-electron integrals, and obviously S(P) can be expressed as a simple product of one-electron overlap integrals.

Thus the matrices

$$(i|h|j) = \int \phi_i^*(\vec{r}_1)\ h_1 \phi_j(\vec{r}_1) d\vec{r}_1 \tag{34}$$

$$(i|j) = \int \phi_i^*(\vec{r}_1)\ \phi_j(\vec{r}_1) d\vec{r}_1 \tag{35}$$

and

$$(ij|1/r|k\ell) = \int \phi_i^*(\vec{r}_1)\ \phi_j^*(\vec{r}_2)\ \frac{1}{r_{12}}\ \phi_k(\vec{r}_1)\phi_\ell(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \tag{36}$$

can be calculated and stored, and the necessary elements combined to make H(**P**) and S(**P**) for a given **P**.

Expanding in terms of the coordinates (Eq. 1), the one-electron integral $(i|h|j)$ separates into a kinetic energy integral and two nuclear attraction integrals,

$$(i|h|j) = \left(i\left| -\frac{1}{2}\nabla^2\right| j\right) - \frac{2}{R}(Z_A + Z_B)\left(i\left|\frac{\xi}{(\xi^2-\eta^2)}\right|j\right)$$
$$+ \frac{2}{R}(Z_A - Z_B)\left(i\left|\frac{\eta}{(\xi^2-\eta^2)}\right|j\right) . \tag{37}$$

With the form of the wave function (6), all the one-electron integrals may be expressed in closed form in terms of the functions (Kotani, 1963)

$$A_n(\delta) = \int_1^\infty t^n \exp[-\delta t]\ dt \tag{38}$$

$$B_n(\alpha) = \int_{-1}^1 t^n \exp[-\alpha t]\ dt \quad . \tag{39}$$

The integrals for non-zero ν may be compactly handled if the definitions of (38) and (39) are extended to

$$A_n^{\nu}(\delta) = \sum_{k=0}^{|\nu|} \binom{|\nu|}{k} (-1)^{\nu-k} A_{n+2k}(\delta) \qquad (38')$$

$$B_n^{\nu}(\alpha) = \sum_{k=0}^{|\nu|} \binom{|\nu|}{k} (-1)^{k} B_{n+2k}(\alpha) \quad . \qquad (39')$$

Then, by direct substitution of the function (6), followed by separation of variables and integration over φ, it may be found that

$$(i|j) = \frac{\pi R^3}{4} \delta(\nu_i, \nu_j) \left[A_{n+2}^{\nu}(\delta)\ B_m^{\nu}(\alpha) - A_n^{\nu}(\delta)\ B_{m+2}^{\nu}(\alpha)\right] \qquad (40)$$

$$\left(i\left|\frac{\xi}{(\xi^2-\eta^2)}\right|j\right) = \frac{\pi R^3}{4} \delta(\nu_i, \nu_j)\ A_{n+1}^{\nu}(\delta)\ B_m^{\nu}(\alpha) \qquad (41)$$

$$\left(i\left|\frac{\eta}{(\xi^2-\eta^2)}\right|j\right) = \frac{\pi R^3}{4} \delta(\nu_i, \nu_j)\ A_n^{\nu}(\delta)\ B_{m+1}^{\nu}(\alpha) \qquad (42)$$

where $n = n_i + n_j$, $m = m_i + m_j$, $\delta = \delta_i + \delta_j$, $\alpha = \alpha_i + \alpha_j$ and $\nu = \nu_i = \nu_j$.

The kinetic energy integral is more tedious, but after some manipulation can be converted to the form

$$\left(i\left|-\frac{1}{2}\nabla^2\right|j\right) = -\frac{1}{8}\delta(\nu_i, \nu_j) \int d\vec{r} \left(\frac{2\rho}{R}\right)^{2|\nu|}$$
$$\times \left[\phi_i^{\circ}\ \nabla^2\phi_j^{\circ} + \phi_j^{\circ}\nabla^2\phi_i^{\circ} - 2\nabla\phi_i^{\circ} \cdot \nabla\phi_j^{\circ} - 4\left(\frac{\nu}{\rho}\right)^2 \phi_i^{\circ}\phi_j^{\circ}\right]$$

where $\phi_i^{\circ} = \zeta^{n_i}\ \eta^{m_i} \exp[-(\delta_i\zeta + \alpha_i\eta)]$, and after substitution of (6)

becomes

$$(i| -\frac{1}{2}\nabla^2|j)$$

$$= \frac{\pi R^3}{4}\,\delta(\nu_i,\nu_j)\times\left[-\frac{1}{2R^2}\right]\Big[\Big\{\delta'^2 A^{\nu}_{n+2}(\delta) - 2(\delta' n' + \delta)A^{\nu}_{n+1}(\delta)$$

$$+ 2\delta' n'\, A^{\nu}_{n-1}(\delta) + (n-n'^2)\, A^{\nu}_{n-2}(\delta)\Big\}\, B^{\nu}_{m}(\delta) \qquad (43)$$

$$-\Big\{\alpha'^2 B^{\nu}_{m+2}(\alpha) - 2(\alpha' m' + \alpha)B^{\nu}_{m+1}(\alpha) + 2\alpha' m' B^{\nu}_{m-1}(\alpha) + (m-m'^2)B^{\nu}_{m-2}(\alpha)\Big\}A^{\nu}_{n}(\delta)$$

$$+\Big\{n'^2 + n - \delta'^2 - m'^2 - m + \alpha'^2\Big\}A^{\nu}_{n}(\delta)B^{\nu}_{m}(\alpha) - 4\nu^2\Big\{A^{\nu-1}_{n+2}(\delta)B^{\nu-1}_{m}(\alpha) - A^{\nu-1}_{n}(\delta)B^{\nu}_{m+2}(\alpha)\Big\}\Big]$$

where $n' = n_i - n_j$, $m' = m_i - m_j$, $\delta' = \delta_i - \delta_j$, and $\alpha' = \alpha_i - \alpha_j$. The coefficients of $A^{\nu}_{n}(\delta)$ and $B^{\nu}_{m}(\alpha)$ vanish when negative indices would be required, and correct results are obtained when these undefined values of A^{ν}_{n} and B^{ν}_{m} are assumed to be zero.

The symmetrized orbitals (6') are easily included by noting that

$$(i_{g,u}|\underline{O}|j_{g,u})$$

$$= (i|\underline{O}|j) + (-1)^{k_i+k_j}(i'|\underline{O}|j') + (-1)^{k_j}(i|\underline{O}|j') + (-1)^{k_i}(i'|\underline{O}|j)$$

where i' is the function $\emptyset(\delta,-\alpha;nm\nu)$. It is clear that

$$B^{\nu}_{m}(-\alpha) = (-1)^m B^{\nu}_{m}(\alpha)$$

therefore it is possible by collecting terms to define the auxiliary integral

$$B'^{\nu}_{m}(\alpha,\alpha') = 2\delta\left[0, m+k_i+k_j (\mathrm{mod}\ 2)\right]\left\{B^{\nu}_{m}(\alpha) + (-1)^{k_j}B^{\nu}_{m}(\alpha')\right\}$$

and since in each of the integrals (40-43) all terms involving m are of the same parity, the Kronecker delta function can be factored out, leaving the integrals in exactly the same form, except using

$B_m^{\prime\nu}(\alpha,\alpha')$ rather than $B_m^{\nu}(\alpha)$. This method is not unique, but it has the advantages that it requires less memory storage, and reduces the amount of actual computation by about one-third.

The $A_n(\delta)$ are obtained by the recursion formula

$$A_n(\delta) = A_o(\delta) + \frac{n}{\delta} A_{n-1}(\delta) \tag{44}$$

with $A_o(\delta) = 1/\delta\ e^{-\delta}$. The $B_m(\alpha)$ could also be generated recursively, using the formula (Kotani, 1963)

$$B_m(\alpha) = \frac{1}{\alpha} \left\{ (-1)^m e^{\alpha} - e^{-\alpha} + nB_{n-1}(\alpha) \right\}$$

but Corbato (1956) has developed a method which does not involve subtraction of terms of similar magnitude and therefore is more accurate. The B_m are calculated in conjunction with related functions used in the two-electron integrals.

Because all the orbitals in this problem are of a single parametric form, there is but one type of 2-electron integral in our work, rather than the usual plethora of hybrid, coulomb, exchange, and one-center integrals. To evaluate the 2-electron integral $(ij|1/r|k\ell)$, we use Neumann's expansion (1878) of $1/r_{12}$,

$$\frac{R}{2r_{12}} = \sum_{u=0}^{\infty} \sum_{\sigma=-\mu}^{\mu} (-1)^{\sigma} (2\mu + 1) \left[\frac{(\mu-|\sigma|)!}{(\mu+|\sigma|)!}\right]^2$$
$$\times P_\mu^{|\sigma|}(\xi_-)Q_\mu^{|\sigma|}(\xi_+)P_\mu^{|\sigma|}(\eta_1)P_\mu^{|\sigma|}(\eta_2)\exp\left[i\sigma(\varphi_1 - \varphi_2)\right], \tag{45}$$

where ξ_+ and ξ_- mean the larger, and smaller, respectively, of

ξ_1 and ξ_2. $P_\mu^{|\sigma|}$ and $Q_\mu^{|\sigma|}$ are associated Legendre functions.

On substituting Eq. (45), and introducing the wave functions, Eq. (6), we perform first the integrations over φ_1 and φ_2. If we let

$$\nu_\kappa - \nu_i = \sigma_1 ,$$

$$\nu_\ell = \nu_j = \sigma_2 \tag{46}$$

the φ dependence of the integral is $\exp i(\sigma_1+\sigma)\varphi_1 + i(\sigma_2-\sigma)\varphi_2$, so the integral vanishes unless

$$\sigma_1 + \sigma_2 = 0 , \tag{47a}$$

in that case the sum over σ collapses to the single value (or its negative)

$$\sigma = |\sigma_1| = |\sigma_2| . \tag{47b}$$

Henceforth we shall use σ to mean the value given by Eqs. (47a)-(47b). The φ integrations then cause the removal of the σ summation, and the change of the lower limit of the μ summation to σ, while contributing to $(ij|1\ r|k\ell)$ a factor $4\pi^2\delta(\sigma_1,-\sigma_2)$.

We next consider the factors involving (ξ^2-1) and $(1-\eta^2)$. When the contributions from all four wave functions are collected, we have

$$\left[\left(\xi_1^{\,2}-1\right)\left(1-\eta_1^{\,2}\right)\right]^{\frac{1}{2}|\nu_i|+\frac{1}{2}|\nu_\kappa|}\left[\left(\xi_2^{\,2}-1\right)\left(1-\eta_2^{\,2}\right)\right]^{\frac{1}{2}|\nu_j|+\frac{1}{2}|\nu_\ell|} .$$

When we do the ξ and η integrations, we will find it convenient to write this as

$$\left[\left(\xi_1^{\,2}-1\right)\left(1-\eta_1^{\,2}\right)\right]^{\frac{1}{2}\sigma+\tau_1}\left[\left(\xi_2^{\,2}-1\right)\left(1-\eta_2^{\,2}\right)\right]^{\frac{1}{2}\sigma+\tau_2} ,$$

since the $1/2\sigma$ power can be naturally associated with the Legendre functions. In general, the τ value to be associated with any two orbitals, say $\emptyset_u$ and $\emptyset_v$, will be $\tau = 1/2(|\nu_u|+|\nu_v|-|\nu_u-\nu_v|)$, and in particular

$$\tau_1 = \frac{1}{2}\left(|\nu_i|+|\nu_\kappa|-\sigma\right)$$
$$\tau_2 = \frac{1}{2}\left(|\nu_j|+|\nu_\ell|-\sigma\right) \quad . \tag{48}$$

Note that these definitions imply that τ is a positive integer or zero.

We are now prepared to consider the integrations over ξ_1 and ξ_2. It is evident that the integrand cannot be factored to separate the coordinates (ξ_1, η_1) from (ξ_2, η_2) because of the presence of the Legendre functions involving ξ_+ and ξ_-. This situation can be alleviated somewhat by using a slight generalization of a formula published by Ruedenberg (1951). The formula we need can be expressed as

$$(-1)^\sigma(2\mu+1)\int_1^\infty d\xi_1 \int_1^\infty d\xi_2 P_\mu{}^\sigma(\xi_-)Q_\mu{}^\sigma(\xi_+)g_\mu{}^1(\xi_1)g_\mu{}^2(\xi_2)$$
$$= \int_1^\infty dX G_\mu{}^1(X)G_\mu{}^2(X) \tag{49}$$

where $g_\mu{}^\gamma(\xi)$ and $G_\mu{}^\gamma(X)$, γ = 1 and 2, are related by

$$G_\mu{}^\gamma(X) = \left\{(2\mu+1)\left[(\mu+\sigma)!/(\mu-\sigma)!\right]\right\}^{\frac{1}{2}}$$
$$\times\left[P_\mu{}^\sigma(X)(X^2-1)^{\frac{1}{2}}\right]^{-1}\int_1^X d\xi P_\mu{}^\sigma(\xi)g_\mu{}^\gamma(\xi). \tag{50}$$

This transformation may be applied whenever all the operations indicated are meaningful. The exponential dependence of the wave functions is sufficient to guarantee the utility of Eqs. (49) and (50).

Summing both sides of Eq. (49) from $\mu = \sigma$ to ∞, we have, with suitable definition of $g_\mu{}^\gamma(\xi)$, an expression for $(ij|1/r|k\ell)$. Examining the result of the substitution of Eqs. (45) and (6) into $(ij|1/r|k\ell)$, it may be seen that

$$g_\mu{}^\gamma(\xi) = [(\mu-\sigma)!/(\mu+\sigma)!] \int_{-1}^{1} d\eta(\xi^2-\eta^2)\exp(-\delta_\gamma\xi-\alpha_\gamma\eta)$$

$$\times \mathbf{P}_\mu{}^\sigma(\eta)(\xi^2-1)^{(\sigma/2)+\tau_\gamma}\,(1-\eta^2)^{(\sigma/2)+\tau_\gamma}\xi^{n_\gamma}\eta^{m_\gamma} \tag{51}$$

Here, $\delta_1 = \delta_i + \delta_k$, $\delta_2 = \delta_j + \delta_\ell$, with corresponding definitions for α_γ, n_γ, and m_γ. The η integrations appearing in Eq. (51) are all of the same general form. Define

$$i_\mu{}^\sigma(m,\alpha,\tau) = \left\{(2\mu+1)\,[(\mu-\sigma)!/(\mu+\sigma)!]\right\}^{\frac{1}{2}}$$

$$\times \int_{-1}^{1} d\eta\,\mathbf{P}_\mu{}^\sigma(\eta)\,\exp(-\alpha\eta)\eta^m(1-\eta^2)^{(\sigma/2)+\tau} \tag{52}$$

and Eq. (51) may be rewritten

$$\begin{aligned}&\left\{(2\mu+1)\,[(\mu+\sigma)!/(\mu+\sigma)!]\right\}^{\frac{1}{2}} g_\mu{}^\gamma(\xi)\\ &\quad= \exp(-\delta_\gamma\xi)\xi^{n_\gamma}(\xi^2-1)^{(\sigma/2)+\tau_\gamma}\left[\xi^2 i_\mu{}^\sigma(m_\gamma,\alpha_\gamma,\tau_\gamma)-i_\mu{}^\sigma(m_\gamma+2,\alpha_\gamma,\tau_\gamma)\right]\end{aligned} \tag{53}$$

The integrals defined in Eq. (52) are related to spherical Bessel functions, and also to the $B_n(\alpha)$. The B_n can be expressed (Corbato, 1956) in terms of the $i_\mu{}^\sigma$ as

$$B_n = \sum_{\mu=0,1}^{n}{}' \frac{n!\,(2_{\mu+1})^{\frac{1}{2}}}{(n-\mu)!!(n+\mu+1)!!} \; i_\mu(0,\alpha,0) \tag{54}$$

where $\sigma = 0$, or if $\nu \neq 0$, since σ is necessarily zero for non-zero one-electron integrals, $\nu_i = \nu_j = \tau$, so the binomial summation of (39') can be avoided by using the relation

$$B_n^{\nu}(\alpha) = \sum_{\mu=0,1}^{n}{}' \frac{n!\,(2_{\mu+1})^{\frac{1}{2}}}{(n-\mu)!!(n+\mu+1)!!} \; i_\mu(0,\alpha,\tau) \; . \tag{54'}$$

In both expressions the prime on the summation sign indicates taking only every other term such that the highest μ value = n, and the double factorial is $n!! = n(n-2)(n-4)\ldots(2 \text{ or } 1)$.

For the symmetrized one electron orbitals, the $i_\mu^{\sigma}(m,\alpha,\alpha',\tau)$ become

$$i_\mu^{\sigma}(m,\alpha,\,\alpha',\tau) = 2\delta_{[0,\mathrm{mod}_2(m+\kappa_i+\kappa_j+\mu-\sigma]}\left\{i_\mu^{\sigma}(m,\alpha,\tau)+(-1)^{\kappa_j} i_\mu^{\sigma}(m,\alpha',\tau)\right\} \tag{55}$$

since

$$P_\mu^{\sigma}(-\eta) = (-)^{\mu-\sigma}\; P_\mu^{\sigma}(\eta) \; .$$

The next step is to substitute Eq. (53) into Eq. (50), and perform the ξ integration. When doing so, it is convenient to define another set of integrals

$$K_\mu^{\sigma}(n,\delta,\tau,X) = \left[P_\mu^{\sigma}(X)(X^2-1)^{\frac{1}{2}}\right]^{-1} \times \int_1^X d\xi\, P_\mu^{\sigma}(\xi)\exp(-\delta\xi)\,\xi^n(\xi^2-1)^{(\sigma/2)+\tau} \tag{56}$$

in terms of which Eqs. (53) and (50) yield

$$G_\mu{}^\gamma(\chi) = K_\mu{}^\sigma(n_\gamma + 2,\delta_\gamma,\tau_\gamma,\chi)i_\mu{}^\sigma(m_\gamma,\alpha_\gamma,\tau_\gamma)$$
$$- K_\mu{}^\sigma(n_\gamma,\delta_\gamma,\tau_\gamma,\chi)i_\mu{}^\sigma(m_\gamma + 2,\alpha_\gamma,\tau_\gamma) \ . \qquad (57)$$

To show more clearly the role of the wave functions in $G_\mu{}^\gamma(\chi)$, we shall from now on use the notation $(u|G_\mu(\chi)|v)$ to mean a form like $G_\mu{}^\gamma(\chi)$, but with n_γ replaced by $n_u + n_v$, etc.

Recapitulating the earlier discussion in more explicit form, we obtain the result that the two-electron integral has been reduced to the form

$$(ij|1/r|k\ell) = \left(\frac{\pi R^3}{4}\right)^2\left(\frac{2}{R}\right)\delta(\sigma_1,-\sigma_2)\int_1^\infty d\chi\sum_{\mu=\sigma}^{\infty}(i|G_\mu(\chi)|k)(j|G_\mu(\chi)|\ell). \qquad (58)$$

The integral over χ in Eq. (58) is now to be evaluated numerically. Using values of the integrand at points χ_κ, the integral can be written

$$(ij|1/r|k\ell) = \left(\frac{\pi R^3}{4}\right)^2\left(\frac{2}{R}\right)\delta(\sigma_1,-\sigma_2)\sum_\kappa w_\kappa\sum_{\mu=\sigma}^{\infty}(i|G_\mu(\chi_\kappa)|k)(j|G_\mu(\chi_\kappa)|\ell),$$

where w_κ is a weight factor. Defining

$$(w_\kappa)^{\frac{1}{2}}\ (i|G_\mu(\chi_\kappa)|j) = (i|G_{\mu\kappa}|j), \qquad (59)$$

Eq. (58) becomes

$$(ij|1/r|k\ell) = \left(\frac{\pi R^3}{4}\right)^2\left(\frac{2}{R}\right)\delta(\sigma_1,-\sigma_2)\sum_\kappa\sum_{\mu=\sigma}^{\infty}(i|G_{\mu\kappa}|k)(j|G_{\mu\kappa}|\ell) \ . \qquad (60)$$

The number of terms one must keep in the sum over μ may be estimated by studying the behavior of the K and i integrals, Eqs. (52) and (54). By far the most important quantities affecting the convergence of the sum are found to be $|\alpha_1|$ and $|\alpha_2|$, larger values of which correspond to slower convergence. In fact, for $\alpha = 0$ the series reduces to a finite number of terms. Since the speed of computation depends on the number of terms, we actually compute a number chosen for each integral after examining its $|\alpha_1|$ and $|\alpha_2|$. As a rough indication, we use an average of 13 terms for $|\alpha| = 10$, and 19 terms for the maximum value, $|\alpha| = 19.9$.

Details of the calculation of the integrals $i_\mu^{\sigma}(m,\alpha,\tau)$ and $K_\mu^{\sigma}(n,\delta,\tau,x)$ can be found in Appendices II and III of the Harris work (1960).

Parameter Variation Scheme

The trial wave function can be improved both by selection of the best set of linear coefficients through diagonalization of the secular equation, and by minimization of the energy with respect to the non-linear parameters δ_i and α_i, $i = 1,2, \ldots N_{\emptyset}$. In this discussion, the word energy signifies the total electronic energy of the desired root of the secular equation.

In the earlier modifications of the diatomic program, a pure network search was used, because there was no way of knowing at that time whether more sophisticated searching routines would get trapped in false minima.

An analysis of the energy dependence on the non-linear parameters has now become possible since large numbers of calculations on many types of systems have been performed using the stepwise search.

Several representative calculations have been analyzed, including ground states, excited states, heteronuclear and homonuclear molecules, atoms, and resonant states. Some definite features were observed, leading to the following conclusions:

1. In true bound states of atoms or molecules, both ground and excited, the dependence of the energy on the non-linear parameters is smooth. No false or pseudo-minima were found in any of the extensive number of calculations checked.
2. The energy is considerably more sensitive to the choice of the δ parameter for a given orbital than the choice of the α of the same orbital.
3. The parameters of the orbitals, if originally chosen in a "reasonable" fashion (not such that the maximum density of a $\sigma 2s$ lies inside the maximum density of a $\sigma 1s$, for example), are relatively independent of each other.
4. Resonant states exhibited false minima in the δ parameter of the added electron (outermost orbital), and the α dependence was nearly flat. The energy is particularly sensitive to very small variations of δ in the region nearest the minimum.

Thus it is now possible to use a more sophisticated parameter searching routine, as long as some option is retained to avoid the false minima in resonances (or other false minima if they are suspected).

Consider the case of a set of parameters chosen so that the energy is near the minimum value attainable with the trial function being used. Let x_i represent the non-linear parameters, either δ_i or α_i, E_o = the energy calculated with the set x_i, and y_i the set of increments $(x_i - a_i)$. The energy can be expanded as

$$E_x = E_o + \sum_i \left(\frac{\partial E}{\partial x_i}\right)_o y_i + \frac{1}{2} \sum_i \sum_j \left(\frac{\partial^2 E}{\partial x_i \partial x_j}\right)_o y_i y_j + \ldots \qquad (61)$$

and the minimum will be attained if

$$\frac{\partial E}{\partial x_i} = 0 \qquad (62)$$

Dropping all terms of order greater than two in the expansion and substituting the minimization condition, we obtain the set of equations

$$\left(\frac{\partial E}{\partial x_i}\right) + \sum_j \left(\frac{\partial^2 E}{dx_i dx_j}\right) y_i = 0 \qquad (63)$$

which can be solved for the revised set of parameters if 1/2(n+2)(n+1) calculations of the energy are done (n is the number of parameters in the set $\bar{x}_i$). This can be seen to be the equivalent of assuming the energy dependence on each parameter to be a parabola, and finding the minimum of the set of parabolae which are linked by the cross terms

$x_i x_j (i = j)$. Ransil (1960) applied a similar procedure to diatomic molecule calculations and found that if the parameters were nearly independent, this method converged in three to five passes through the set of $1/2(n+2)(n+1)$ energy calculations, using the new $\overline{y}_i$ to determine a revised E_o.

However, if the parameters are independent, or nearly so, the effect of the cross terms should be negligible, and an equivalent result should be obtained if each of the parameters $\overline{x}_i$ were fitted to a parabola holding the other parameters fixed, and the set $\overline{x}_i$ stepped through one by one. This requires only 3n energy calculations per pass through the set $\overline{x}_i$, and as there are two non-linear parameters per orbital, produces a nice reduction in the amount of work necessary to minimize the energy with respect to the non-linear parameters if there are two or more orbitals.

This process, with a slight modification to be described below, is the one used in the present diatomic program. It also converges quite rapidly, with two passes normally minimizing the energy to five or six figures.

The actual scheme works slightly differently for variation of $\overline{\delta}_i$ and of $\overline{\alpha}_i$. Since the initial set of δ parameters may be quite far from the optimum set, each parameter is stepped with a large step size in the forward or backward direction until there exists an $E_i(\delta_i)$ which is less than both $E_{i-1}(\delta_{i-1})$ and $E_{i+1}(\delta_{i+1})$, where i indexes the number of the calculation. If the energy continues to improve in a certain direction, the step size is increased to hasten finding

the δ_{i+1} which causes the energy to turn back upwards. The optimum parameter δ is then determined by fitting to the parabola passing through the lowest three points E_i, E_{i+1}, and E_{i-1}. In this process, more than three energy calculations may be required before fitting, but it has the advantage that the first pass through the δ set always produces a revised E_o which is quite close to the true minimum of the functional.

Since the α dependence is more flat, the search procedure for the first pass through the α parameters only makes three calculations per α, at the values α_o, $1/2\ \alpha_o$, and $3/2\ \alpha_o$. On subsequent passes through the α set, the method is the same as for δ.

After one complete pass through all the δ and α which are to be optimized, the step size is reduced to one-third the starting value and the process is repeated.

In the case of resonances, a stepwise search over the parameters of the outermost electron is still necessary in order to avoid becoming trapped in a pseudo-minimum. This option is included in the program by setting a tag which both demands a stepwise search in the forward direction, and determines the number of steps to be taken. As in the previous modifications of the program, the programmer-user must apply his experience and physical intuition to determine the magnitude of the step size and the number of steps which will locate the parameter near the true minimum without becoming trapped. After each of the designated outer orbital parameters has been linearly searched by this method, the optimum set of stepwise parameters is

re-minimized by the parabola search method.

In all of the above procedures, the search may be terminated externally by setting of a sense switch. In the parabolic search, variation of a particular parameter is eliminated in subsequent passes if the program determines that the energy is relatively independent of it. This can also be done externally by proper preparation of the input cards.

If the program is not terminated externally, it proceeds automatically through the list of parameters to be varied, reducing the step size after each pass until it is lower than a preset threshold step size. At this time, a final calculation is made with the optimum set of parameters and the search for the problem is terminated.

In this modification of the program, it is also possible to treat the internuclear distance R as a parameter, in that after completion of a parameter search at one R value, R can be incremented or decremented and the problem restarted. In this case, the non-linear parameters are scaled by R_{new}/R_{old}, and the $\bar{\alpha}$ search assumes that it has already made one pass.

Thus, if computer time is available, it is possible to calculate the entire potential curve for a particular molecule in one run, stepping through R and minimizing the energy in terms of the non-linear parameters at each desired R value.

APPENDIX II. DETAILS OF THE DIATOMIC MOLECULE PROGRAM AND INSTRUCTIONS FOR ITS USE

Overall Logic

General Comments

The diatomic molecule program as written is designed for a 32,768 word high-speed computer with at least four peripheral storage units (tape or disc). It is in the FORTRAN IV language, with no machine language programs, in order that maximum machine-to-machine compatibility be achieved. To the same end, no advantage has been taken of special features of some machines, such as reading tapes backward, multiple entries to subroutines, availability of additional peripheral equipment, etc. Variable dimension statements and logical IF statements have been used.

A rather extensive list of options has been included, in order to do the most general diatomic molecule problem without changing the program internally, and still allow some special treatment of specific problems.

The program is designed to calculate the energy and electronic wavefunction of heteronuclear or homonuclear diatomics. In the homonuclear case, gerade or ungerade symmetry can be achieved either through the use of symmetry adapted one-electron orbitals, or by an

option of reflecting the entire molecular function through the inversion center and taking the proper linear combination of the original and inverted functions.

The spin portions are set to handle the complete open-shell (different orbitals for different spins) problem automatically for up to a 28×28 set of representation matrices, which includes the full eight electron case. By a change in the input deck, up to twenty electrons may be handled with partially or completely closed shells. The spin routines are also arranged so that advantage can be taken of the reduction in numbers of permutations which can be introduced through spatial orthogonalities, by never generating those permutations which would make no contribution to the secular equation.

The one-electron spatial functions are two-centered elliptical orbitals. A transformation routine is included which allows linear combinations of these functions prior to diagonalization, so that both fixed and variable linear coefficients are possible. Space is available for up to sixteen functions and a 16×16 transformation matrix.

Non-linear parameter search options include a combination network-gradient search and a pure stepwise network search, with the ability to vary one function independently, or two functions simultaneously. Through appropriate tagging, one, both, or neither of the two non-linear parameters of a particular function may be varied, and the search routine has the ability to set these tags internally if the energy is found to be relatively independent of the parameter being varied.

Through the use of sense switches, the programmer may also externally terminate the search, skipping immediately to the final output routine with the best set of parameters achieved up to that time.

The internuclear distance may also be varied, with a new calculation of the electronic wave function, including non-linear parameter variation at each R value.

Thus the program presented here is a compromise among generality, speed, efficiency, and size. For selected specific types of problem, some of the options may be removed if desired for further optimization of these factors.

Block Structure

The logic flow of the program is divided into five main branches, which are handled by an input and controlling main program. The function of each of these branches is as follows:

Branch 1 - SETUP Branch

Reads auxilliary tape identifiers, loads permanent data tables for integral calculations, makes spin-permutation tape. Re-entered only if spin problem is changed. All output from this branch is labeled COMMON blocks or on tape (disc).

Branch 2 - INTEGRAL Branch

Controls calculation of all one- and two-electron spatial integrals. Makes integral table tape of indices, parameters, one-electron integrals, and $G_{i,k}(x,\mu)$. Combines all $G_{i,k}$

with $G_{j,\ell}$ to make tape of all two-electron integrals. Upon exit, all one- and two-electron integrals are on tape for subsequent iterations, and in fast memory for combining with spin.

Branch 3 - MATRIX Branch

Applies transformation to spatial integrals if required. Combines spatial integrals with spin matrices from tape to make total secular equation. In homonuclear case with total molecular inversion option, secular equation is block diagonalized in this branch.

Branch 4 - SEARCH Branch

Solves secular equation. Varies non-linear parameters as desired, prints intermediate output. If parameter search not completed, return to INTEGRAL branch, otherwise proceed to OUTPUT branch.

Branch 5 - OUTPUT Branch

Prints final output, including total secular equation, eigenvalues, eigenvectors, converted energies and spatial configurations. If program was cut externally by sense switch, punches new input deck for convenient restart.

Control of Storage and Internal Overlays

Of prime importance is the control of the working space inside fast memory. In the various branches, and inside the branches, data is overlaid when it is no longer needed. In order to prevent destroying information which will be required later in the calculation,

an understanding of the places and times that these overlays occur is mandatory if modifications are to be introduced, if it is desired to use certain routines as "black boxes" for entirely different calculations, or if the program is to be updated.

To facilitate bookkeeping, all fast storage is in four labeled COMMON blocks. A description of the contents of these blocks and the overlays which occur in them follows.

/SPACE/ - 3∅9 words. Contains most problem definition data as described in input deck summary below, plus

ITX - iteration counter. 1-first pass; 2-intermediate passes; 3-final pass

FPAR∅ - best set of non-linear parameters, stored from FPAR as determined

E∅ - best energy, corresponding to calculation with FPAR∅

NO - tag for parameter being searched. 1-delta; 2-alpha

MO - function number of parameter being searched, i.e., search over FPAR(NO,MO)

ICTAG - 64 locations available for additional tags as desired.

Data in this block is generally permanent, with the only overlays being resetting of tags, changing parameters, etc.

/DATBLS/ - 759 words. Permanent information. Not changed during run. See below for details.

/CIJ/ - 268 words. Transformation matrix and tags. Matrix is recalculated if NOTRF > ∅, but not overlaid by other data.

/WORK/ - 12,518 words. Main working area. Overlaid by all branches as follows:

1. SETUP - overlays controlled by subroutine SPIN. Used to contain all information for generation of spin tape. Completely destroyed upon exit from spin routine.
2. INTEGRAL - during making of one-electron tapes and combination to make two-electron tape, /WORK/ is composed of two arrays JTA and JTB, dimensioned 146∅x4, and the one-electron integrals S1 and H1, singly dimensioned at 136 words each. S1 and H1 are stored as calculated. The two-electron tape is read upon completion, storing the H2 integrals over JTA and JTB. Array JTB is used as temporary storage by the integral routines ONEL, BANDI, and GLIST. 289 locations available in array named DUMBO.
3. MATRIX - at entry, contains H2 (9317), SPRI, HPRI (S1, H1 of INTEGRAL branch), transformed one-electron sets renamed S1,H1, one 28x28 spin matrix, one permutation, and room for the total S,H stored triangularly (18∅6 words). At exit, H2 is overlaid by the total secular equation OVP, HAM which is S,H unpacked and stored as full two dimensioned arrays. Array named DOM has 19 locations available.
4. SEARCH - six 42x42 matrices for secular equation and eigenvectors, including two copies of secular equation, one for printing if desired, and one which is destroyed during diagonalization. Several vectors dimensioned 42 for

eigenvalues, etc. Array named FINK has 176∅ locations available.

5. OUTPUT - essentially same as SEARCH, except FINK contains only 1672 locations.

Limitations

The following limitations must be observed to prevent premature termination of the calculation by built-in error checks:

Maximum number of one-electron functions	16
Maximum number of electrons in IPER	20
Maximum number of spin eigenfunctions θ	28
Maximum number of spin functions Ω	--
Maximum dimension of secular equation	42
Largest n_i, m_i	4
Largest α_i	19.9
Smallest δ_i	.01

Error Messages

Error messages may occur during calculation if the internal checks are positive. Some of these errors will not cause premature termination of the program, and others will. The following is a summary of these error messages, their causes, and the action taken by the program:

1. WRONG PERM TAPE xxxxxx xxxxxx

   The identification tag on the spin-permutation tape does not agree with the tag required by the formula

JCODE = 1000*N + 10*10SH + MULT

calculated when the problem is defined. This can be due to a mis-positioned tape or to having mounted the wrong tape. The program repositions the tape and either continues or exits, depending on the condition of a recheck. The first number in the message is the desired number, and the second is the number read from the tape.

2. SEC EQN TOO BIG xxxx

   The dimension of the secular equation requested by the input parameters (NCON×ND) is larger than 42.

3. INDICES DONT CHECK xx xx xx xx xx xx

   Subroutine INTEG has detected that the indices on tape KR and the indices in the integral calculation loop do not correspond. The indices L1, I and J are printed in pairs with the supposed L1, I, and J read from tape KR.

4. BANDI - NO CONVERGE

   The μ summation of Eq. (60) did not converge in 36 terms or less.

5. BANDI - PARAMS OUT xx xx xx xx

   One or more parameters are out of range. The four numbers printed are τ, m, $|\sigma|$, and M, where τ, m, and $|\sigma|$ are defined in Appendix I and $M = 28 + |\alpha|/1.95$, which defines a dimension and cannot exceed 60.

6. GLIST - GENERAL ERR

   Self-explanatory

7. GLIST - PARAMS OUT xxxxxx xx xx

Parameters out of range in subroutine GLIST. The three numbers are δ, n, and LM = L4 + n + 2τ + 2, where δ and n are explained in Appendix I, and LM is a calculated dimension which cannot exceed 45.

8. ENERGY.LT.MIN

The calculated energy is lower than the experimental or test energy punched on the title card. An exit is made to the OUTPUT branch, after which a new calculation may be started if more input cards are present.

9. GR.SRCH SEEKS MAX

The gradient or parabola search is seeking a maximum rather than a minimum. This is an information message only.

10. END SRCH OF FCN xx xx

The energy has been found to be independent of a particular parameter, and the tag has been set to discontinue the search of this parameter. Its indices are printed for information.

11. OVRLAP NOT POS DEF xxxxxxx xx xx

The overlap matrix is not positive definite. If it is positive semi-definite, this is an information message only. If the magnitude of the negative diagonal element is less than 10^{-7}, the program assumes that the matrix is numerically positive semi-definite, deletes the row and column corresponding to this element in both the S and H matrices, and

continues. This results in an eigenvalue of 10^{26} which can easily be seen. If the negative diagonal element is greater than 10^{-7} in magnitude, the program makes an error exit.

Specific Programs and Subroutines

A short summary of the programs follows. Those routines which are marked by asterisks are discussed in detail below the summary. The logic of the unmarked routines can be followed without difficulty in the program listings themselves.

TITLE	TYPE	BRANCH	PURPOSE
DIAT	M	MAIN	DATA INPUT & MAIN CONTROLLING PROGRAM
SETUP	S	SETUP	INITIALIZATION OF TABLES, ETC.
TABLE*	S	SETUP	FIXES PERMANENT DATA BLOCK, POINTS, WEIGHTS, ETC.
SPIN*	S	SETUP	PREPARES TAPE OF SPIN-PERMUTATION MATRICES
CONFIG*	S	SETUP	READS CONFIGURATION TABLES INTO LCON (config. array)
HDG	S	MAIN/ OUTPUT	PRINTS TITLE PAGES IN OUTPUT
INTEG*	S	INTEGRAL	CONTROLS PRODUCTION OF ALL SPATIAL INTEGRALS
ONEL*	S	INTEGRAL	MAKES ONE-ELECTRON INTEGRALS FROM BANDI OUTPUT
BANDI	S	INTEGRAL	MAKES B,A,AND I INTEGRALS
GLIST	S	INTEGRAL	MAKES $G_{ik}(x)$ FROM ξ INTEGRATION AND I INTEGRALS
TWOEL	F	INTEGRAL	COMBINES G_{ik} WITH $G_{j\ell}$ TO MAKE $(ij\|1/r_{12}\|k\ell)$
COMBIN	S	INTEGRAL	CONTROLS CALLING OF TWOEL FUNCTION

TITLE	TYPE	BRANCH	PURPOSE
TAPE	S	INTEGRAL	READS AND WRITES INTEGRAL TAPE
MATRIX*	S	MATRIX	COMBINES SPACE AND SPIN PARTS TO MAKE TOTAL SECULAR EQUATION
TXFORM	S	MATRIX	PREPARES TRANSFORMATION MATRIX FOR SPATIAL FUNCTIONS
TRANS	S	MATRIX	APPLIES TRANSFORMATION TO ONE-ELECTRON INTEGRALS
TRX	F	MATRIX	APPLIES TRANSFORMATION TO TWO-ELECTRON INTEGRALS
SEARCH	S	SEARCH	ENERGY CALCULATION AND PARAMETER SEARCH LINK
D23CHO	S	SEARCH	SOLVES GENERAL EIGENVALUE PROBLEM AND ORDERS ROOTS, VECTORS
EIG	S	SEARCH	JACOBI MATRIX DIAGONALIZATION
OUTPUT	S	OUTPUT	PRINTS FINAL OUTPUT
PMA	S	OUTPUT	PRINTS MATRICES AS SQUARE OR TRIANGULAR ARRAYS

*TABLE - FIXES PERMANENT DATA BLOCK, POINTS, WEIGHTS, ETC. Subroutine TABLE generates D1, DD1, and DD2 for BANDI and GLIST. Their definitions are:

$$D1_{i,j} = (i-1)!(2j-1)/[(i-j)!!(i+j-1)!!] \tag{64}$$

$$DD1_{i,j} = [(i+j-2)!(2i-1)/(i-j)!]^{\frac{1}{2}} \tag{65}$$

and

$$DD2_{i,j} = [(i+j-1)(i-j+1)/(4i^2-1)] , \tag{66}$$

and they are calculated recursively.

The numerical quadrature points and weights are read in this routine. They are read as data rather than loaded as a permanent

BLOCK DATA Subroutine to allow the use of several different quadrature formulae, with different numbers of points. Space is available for up to a forty point integration raule. The integral limits $(1,\infty)$ are transformed to $(0,1)$, so the points are in increments of $1/x$ and the weights are

$$w_k = x_i w_i^{\frac{1}{2}}/(x_i^2 - 1)^{\frac{1}{2}} \qquad (67)$$

where

w_k is the value punched on the input cards, WT(K)

x_i is the i^{th} point in POINT

w_i is the tabulated weight from the numerical quadrature rule.

Card decks have been prepared and are available for the original 34-point Newton-Cotes formula used by Harris and Taylor (1963, etc.), and for 16,20,24, and 32 point Gaussian formulae. Table 9 gives a comparison of two-electron integrals for various δ values using these formulae. The 34-point formula should be used in any check calculations which attempt to duplicate the results of the old Taylor-Harris or Taylor calculations.

*<u>SPIN - PREPARES TAPE OF SPIN-PERMUTATION MATRICES</u>. Subroutine SPIN applies the methods described in Appendix I, (84 ff.) to generate the permutations IPER, and their ND×ND representation matrices UMAT(I,J). A given permutation (read or calculated) is applied to the spin product functions ISP, and an ordering vector ISSPM is created such that if the permutation is denoted by P, and P on ISP(I) yields ISP(K), then ISSPM(K) = I. Using this ordering vector,

TABLE 9

COMPARISON OF ANALYTIC AND NUMERICAL
TWO-ELECTRON INTEGRALS

δ	Analytic	32 Pt Gaussian	24 Pt Gaussian	20 Pt G	16 Pt G	34 Pt Newton-Cotes
.005	$.312496 \times 10^{-2}$	$.357119 \times 10^{-2}$	$.382192 \times 10^{-2}$	$.273463 \times 10^{-2}$	$.116467 \times 10^{-2}$	$.114793 \times 10^{-1}$
.010	$.624967 \times 10^{-2}$	$.591432 \times 10^{-2}$	$.669905 \times 10^{-2}$	$.782367 \times 10^{-2}$	$.721512 \times 10^{-2}$	$.114921 \times 10^{-1}$
.02	$.124973 \times 10^{-1}$	$.126405 \times 10^{-1}$	$.120132 \times 10^{-1}$	$.119074 \times 10^{-1}$	$.140510 \times 10^{-1}$	$.118887 \times 10^{-1}$
.04	$.249787 \times 10^{-1}$	$.249477 \times 10^{-1}$	$.251654 \times 10^{-1}$	$.251091 \times 10^{-1}$	$.237301 \times 10^{-1}$	$.181768 \times 10^{-1}$
.08	$.498302 \times 10^{-1}$	$.498276 \times 10^{-1}$	$.498209 \times 10^{-1}$	$.497302 \times 10^{-1}$	$.503481 \times 10^{-1}$	$.505149 \times 10^{-1}$
.16	$.986616 \times 10^{-1}$	$.986615 \times 10^{-1}$	$.986571 \times 10^{-1}$	$.986810 \times 10^{-1}$	$.985717 \times 10^{-1}$	$.996227 \times 10^{-1}$
.25	.151281	.151281	.151282	.151278	.151306	$.150251 \times 10^{-1}$
.32	.189865	.189865	.189864	.189866	.189852	.189674
.5	.277261	.277261	.277261	.277260	.277254	.277393
.75	.367753	.367753	.367753	.367753	.367738	.367721
1.0	.425974	.425974	.425974	.425974	.425957	---
1.5	.479705	.479705	.479705	.479705	.479686	---

$$\mathrm{UMAT(I,L)} = \left[\sum_{J=1}^{NISP} \mathrm{USET(I,J)} \cdot \mathrm{USET(L,K)}\right] \cdot \mathrm{SIG}$$

where USET is the spin eigenvector matrix, K = ISSPM(J), and SIG = ±1, the parity of the permutation P.

*CONFIG - READS CONFIGURATION TABLES INTO LCON. Subroutine CONFIG is simply a reading routine using variable dimension statements which allows maximum use of the 150 words allocated for the configuration table LCON. LCON is dimensioned as an NCON×N matrix rather than with fixed dimensions, so that 75 two-electron, 50 three-electron, etc. configurations are possible. CONFIG reads, prints, or punches LCON in this type of storage. Note, however, that the maximum dimension of the total secular equation is 42×42, and that NCON×ND may not exceed this limit.

*INTEG - CONTROLS PRODUCTION OF ALL SPATIAL INTEGRALS. The second major branch is controlled by subroutine INTEG, which handles the calculation of all spatial integrals. This is done in two steps, the first being the calculation of the one-electron integrals $S1_{ij}$, $H1_{ij}$ and G_{ij} for all i and J $(i \geq j)$, and second, taking all possible combinations of G_{ij} with $G_{i'j'}$ to make the two-electron integrals.

To save storage space, and due to the symmetry of the spatial one-electron matrix elements, the $S1_{ij}$ and $H1_{ij}$ sets are stored as vectors containing only the $\frac{1}{2}n(n+1)$ elements of the lower triangle. The (i,j) element of the matrix can be looked up by

$$\mathrm{INDX(I,J)} = \mathrm{MIN(I,J)} + [(\mathrm{MAX(I,J)} \cdot (\mathrm{MAX(I,J)}-1)]/2$$

where MIN(I,J) is the lesser of i and j, and MAX(I,J) the greater.

By the same token, a double application of this method allows storage of the two-electron integrals in a single vector H2, containing 1/2 m (m+1) elements where m=1/2 n (n+1). In this case, the φ integrations are done later.

A single (i,j) integral table requires 1460 words — 19 words for indices, parameters, and one-electron integrals, and the (40×36) $G_{ij}(x,\mu)$ matrix (also treated as a one-dimensional vector by INTEG — unpacked only in GLIST and TWOEL).

For optimization of input-output time, since these tables (named JTA, JTB, or ZG1 in the routine) must be stored on tape or disc, they are generated in blocks of four, and written on tape KW each time four sets have been completed. One to three blank tables may be written in the last block of four in order to make the total number of tables a multiple of four. If a previous integral tape KR exists (i.e., second and subsequent passes of parameter variation scheme), the pertinent blocks of tables are read from this tape before actual integral calculation begins.

Subroutine ONEL is called for generation of each table. Upon return, the $S1_{ij}$, and $H1_{ij}$ are extracted, normalized, and stored in fast memory for subsequent branches.

The second, combination, stage of INTEG uses COMBIN and TWOEL. Every block of four tables must be combined with every other block, making ten or sixteen two-electron integrals depending upon whether a block is combined with itself or another block.

To effect this combination of G_{ik} tables from the tape, the following logic is used to minimize tape-handling time, which experience has shown to be the rate-controlling step in the entire energy calculation.

Let there be NTOT blocks of four tables. The last (NTOTth) block is still intact in fast memory. This block is combined with itself while the tape is rewound. The tape is then read forward and blocks 1,2,3....., NTOT-1, are combined with NTOT. At this point, the NTOTth block has been completely combined, so NTOT is reduced by one. The tape is now read backwards (actually, two BACKSPACEs followed by a read to remain in the FORTRAN IV language), combining the new NTOTth block with all the blocks down to block one. This process is continued back and forth dropping a block each time as it has been fully combined until all the blocks have been eliminated. For example, if there are five blocks of four tables, the logic would produce the following order of block combination:

55,51,52,53,54,44,34,24,14,11,12,13,33,23,22.

Since the single index of each two-electron integral is calculated from the i,j,k,ℓ indices in the tables and written on the two-electron integral tape KINT along with the integral, this peculiar order of calculation has no effect.

Upon completion of the combinations, the two-electron integrals are read into fast memory for the next branch.

*<u>ONEL - MAKES ONE-ELECTRON INTEGRALS FROM BANDI OUTPUT</u>. Subroutine ONEL is called by INTEG with a particular i and j, and a designated table of 1460 words. ONEL compares the parameters in the

table (if an old table exists) with the current set and either returns if there has been no change, or calculates a new set of one-electron integrals and G vector through calls to BANDI and GLIST.

The layout of each individual table is as follows [Greek symbols as defined in Appendix I (ff.)]:

<u>WORD</u>	<u>DEFINITION</u>
1	NLP(1) - $\nu_i - \nu_j = \sigma$
2	NLP(2) - $(\lvert\nu_i\rvert + \lvert\nu_j\rvert - \lvert\sigma\rvert)/2 = \tau$
3	NLP(3) - $m_i + m_j = m$
4	NLP(4) - number of steps necessary for convergence of I integrals (i.e., upper limit of μ summation)
5	NLP(5) - $n_i + n_j = n$
6	NLP(6) - $m_i - m_j = m'$
7	NLP(7) - $n_i - n_j = n'$
8	NOTA(1) - I
9	NOTA(2) - J
10	EPOT - potential energy term, independent of R
11	INDX - J+I(I-1)/2 ($J \leq I$)
12	Maximum length of table - 19+JMAX·(NLP(4) - [illegible])
13	FLP(1) - $\delta_i + \delta_j = \delta$
14	FLP(2) - $\delta_i - \delta_j = \delta'$
15	FLP(3) - $\alpha_i + \alpha_j = \alpha$
16	FLP(4) - $\alpha_i - \alpha_j = \alpha'$
17	S1(I,J)
18	EKIN - kinetic energy term, independent of R

WORD	DEFINITION
19	GINY - point at infinity for G_{ij}, zero except in 34-point Newton-Cotes integration (see Harris, 1960 - Eq. 115)
20	G_{ij} - integral table, of length JMAX·(NLP(4) - $\|\sigma\|$)

*MATRIX - COMBINES SPACE AND SPIN PARTS TO MAKE TOTAL SECULAR EQUATION. Subroutine MATRIX calls TXFORM and TRANS to prepare the spatial one-electron integrals in final form.

The spatial integrals and the spin matrices are combined to make the secular equation

$$\sum_{P} U(P)\ [H(P) - ES(P)] = 0$$

storing $\underline{H}(P)$ and $\underline{S}(P)$ as row vectors of dimension 1/2 NMAT·(NMAT+1), where NMAT is NCON×ND.

The routine makes one pass through the spin tape, preparing all contributions of a particular permutation matrix to each matrix element in H and S before reading the next set on IPER and UMAT from the tape.

The function TRX is used to look up the proper two-electron integral and apply any transformations to it, plus doing the p integration. It is called with the indices i,j,k,ℓ and returns the integral $(ij|1/r_{12}|k\ell)$.

After the secular equation is complete, it is unpacked and stored as two full matrices, HAM and OVP, for use by the diagonalization and search routines.

In the homonuclear case, if the full molecular inversion option has been selected, the secular equation is pretransformed at this

point into block diagonal form, with two blocks of equal size. The block corresponding to the desired symmetry (g or u) will be in the upper left, and only this block will be carried over into the next branch.

Input Deck Setup

The input deck is divided into three sections:

1. Points and weights for numerical quadrature (SETUP branch)
2. Spin information (SETUP branch)
3. Problem definition and electron information (MAIN branch)

Section 1 is common to all calculations in which a specific quadrature rule is desired, and is retained in memory intact throughout the entire run. Section 2 is common to all calculations involving the same number of electrons and a specific spin multiplet. It is used to produce the spin tape, which is retained until subsequent data cards redefine the spin problem. Section 3 is only common to the calculation which is immediately in progress.

One comment is necessary here. This program was designed to be compatible with any machine which accepts a FORTRAN IV language. Due to differences from system to system, all input-output statements involving tapes (common input tape, work tapes, etc.) use symbolic names. The actual numbers can be read from data cards, with one important exception. The symbolic tag of the common input tape for a particular system must be set internally. Therefore, even though this is not part of the input deck, this is included here. In the main program, the variable IN must be set to correspond to the logical tape

number for the system common input tape. (Example - for the Honeywell Automath 800/1800, IN = 2, for IBM 7094/7044 DCOS, IN = 5).

The setup for the input deck proper is as follows:

BRANCH	CARD NO.	FORMAT	LIST
SETUP	1	(12I3)	KW, KR,NT,KINT,IOUT,NPCH

KW - Write tape for integral tables

KR - Read tape for integral tables

NT - Spin tape

KINT - Two electron integral tape

IOUT - Logical number of system common output tape

NPCH - Logical number of system common punch tape

SETUP	2	(6X,2F8,E30.12,2A6)	JMAX,NMINUS,WTINF,RULE

JMAX - Number of points in quadrature formula

NMINUS - Number of points to be accumulated negatively (See WT below)

WTINF - Weight of point at infinity (= 0 for Gaussian quadratures)

RULE - Alphabetic name of quadrature formula (limited to 12 letters)

SETUP	3-12	(6X,4E18.12)	POINT

POINT - Array of quadrature points (Maximum = 40 points)

SETUP	13-22	(6X,4E18.12)	WT

WT - Array of weights corresponding to points. These contain the square root of the weight given by the quadrature formula. Since some may be negative leading to imaginary roots, only absolute values are stored, with the first MINUS weights being the negative ones.

SETUP	1	(12I3)	JNT,NEL,NISP,MULT,ND,IOSH,JGEN

JNT - Tag.JNT=0, make new spin tape; JNT=1, spin tape already mounted

NEL - Number of electrons

NISP - Number of spin product functions (eigenvalues of S_z)

BRANCH	CARD NO.	FORMAT	LIST

MULT - Spin multiplicity 2S+1

ND - Number of eigenfunctions of S^2 (= dimension of a one-configuration block of the total secular equation)

IOSH - Number of open-shell electrons (See App. I and II)

JGEN - Number of hand-generated permutations (See App. I and II)

SETUP	2(deck)	(14I5)	ISP

ISP - Spin product functions. Read as column vector of dimension NISP

SETUP	3(deck)	(5F14.10)	USET

USET - Coefficient matrix for eigenfunctions of S^2. Dimension ND×NISP, read as column vectors.

SETUP	4(deck)	(F9.4,21I3)	SIG,JPRI,KPRI

SIG - Parity of a hand-generated permutation

JPRI - Hand-generated permutation (Example - +1. 3 4 1 2)

KPRI - Aux. permutation with double occupancies noted

Note - if JNT = 1, card decks 2, 3, and 4 are omitted.

MAIN	1	(8A6,3F10.6)	TITLE,A1,A2,EFIN

TITLE - Run identification of 48 characters, to be printed on each output page

A1 - Atomic energy of atom 1

A2 - Atomic energy of atom 2 (A1,A2 used to calculate dissociation energy)

EFIN - Experimental energy. If $E_{calc} < E_{fin}$, the program assumes an error exists and stops. If no error test is desired, set EFIN = 0.

MAIN	2	(7F10.4)	ZA,ZB,RMAX,STEP3,STEP2,RMIN,RSTEP

ZA - Nuclear charge of atom A

ZB - Nuclear charge of atom B

RMAX - Maximum internuclear separation.

STEP3 - Maximum step size in variation of non-linear parameters

STEP2 - Minimum step size in variation of non-linear parameters

BRANCH	CARD NO.	FORMAT	LIST

RMIN - Minimum internuclear separation. If blank, only RMAX is used.

RSTEP - Decrement to RMAX until R $\leq$ RMIN

MAIN	3	(12I3)	N,NHUG,NCON,NFCN,NPC,NE,LSRCH, NOTRF,NU,KOLD,IS

N - Number of electrons (used as check on NEL and spin tape) .

NHUG - Tag. 0 = Heternuclear; ±1 = Homonuclear with symmetrized orbitals; ±2 = Homonuclear with inversion of total molecule; > 0 = gerade, < 0 = ungerade.

NCON - Number of spatial configurations

NFCN - Number of spatial functions

NPC - Number of functions whose parameters are to be varied. For single calculation, set = 0.

NE - Eigenvalue to be minimized. 0 = ground state, 1 = 1^{st} excited state, etc.

LSRCH - Search tag. 0 = standard step and gradient search. > 0 = linear search of LSRCH steps in positive direction.

NOTRF - Spatial transformation tag. < 0, read C_{ij} from cards; = 0, no transformation; = 1, project out first NU functions from specified orbitals; = 2, orthonormalize all spatial functions.

NU - See NOTRF. If NOTRF = 0, NU can be used to start parameter search in NU + 1^{st} spatial function.

KOLD - Variation tag. = 0, vary each spatial function independently; = 1, vary i and i + NFCN/2 simultaneously.

IS - Search tag. 0 = search α as 3/2 α, α, 1/2 α, $\geq$ 2 search α as δ. (Special note: if an old integral tape KR exists, IS = 2 will set ITX = 2. This provides a convenient restart if the last KW tape has been saved.)

MAIN	4(deck)	(I5,2F10.6,6I3)	I,FPAR(1,I),FPAR(2,I),(NFPAR(J,I), J=1,6)

Spatial function cards

I - Function number

FPAR(1,I) - δ_i

FPAR(2,I) - α_i

NFPAR(1,I) - n_i

BRANCH	CARD NO.	FORMAT	LIST

NFPAR(2,I) - m_i

NFPAR(3,I) - ν_i

NFPAR(4,I) - Parity of symmetrized orbital 0 = gerade, + 1 = ungerade

NFPAR(5,I) - Projection tag. = 0 - no projection; = 1, project out 1^{st} NU functions

NFPAR(6,I) - Variation tag. = 0, search both δ and α; = 1, search α only; = 2, search δ only; = 3, no search of this function

MAIN	5(deck)	(12I3)	I,(LCON(I,J),J=1,N)

I - configuration number

LCON - Array of function numbers belonging to the configurations

MAIN	6(deck)	(6E12.7)	((C(I,J),J=1,N),I=1,N)

C - Transformation matrix for spatial functions. No deck unless NOTRF = -1

APPENDIX III. ILLUSTRATIVE EXAMPLES AND HINTS - THE NO^+ CALCULATION

Illustrative examples are furnished to allow the reader to see just how an input deck is set up for a particular type of problem, and as calculations which can be used to check that the program is running properly on a particular computer after the minor modifications necessary to make it compatible with that computer have been made.

Three problems are listed in the sample input decks of Table .
The first of these is a LiH calculation, illustrating the heteronuclear capability of the program. This is a one-configuration four electron singlet calculation, and the correct results for the lowest root are:

1. Total electronic energy = -9.708228 au
2. Electronic + nuclear (potential curve) = -7.708228 au
3. Dissociation energy = -7.708228 au

The input deck for this run is self-explanatory once the summary in Appendix II is understood.

The second example is an H_2 calculation using the symmetrized one electron orbitals and two configurations, $C_1\sigma_g 1s\sigma_g 1s' + C_2\sigma_u 1s\sigma_u 1s'$.
This is for the ground state and the calculated energies should be:

1. Total electronic energy = -1.869461 au

2. Electronic + nuclear (potential curve) = -1.155176 au

3. Dissociation energy = - .155176 au

Note that NHUG = +1 for a gerade state with symmetrized orbitals.

Third, the H_2 calculation is repeated using the option of total inversion of the molecule through the inversion center, selecting the gerade linear combination $\Psi + i\Psi$. Several things should be noted here. The first is that the reflected counterpart of each function (same function with α replaced by $-\alpha$) is included explicitly in the input deck, and that all unreflected functions precede the reflected ones so that if there are m unreflected functions 1,2,...m, and each corresponding reflected function is denoted $1',2',...m'$, the input functions are numbered 1,2,....,m, m+1 = $1'$, m+2 = $2'$,....., m+m = m'. The configuration cards are treated similarly, in that each configuration cards are treated similarly, in that each configuration made of unreflected orbitals must be paired with a configuration composed of the corresponding reflected orbitals, with all unreflected configurations. The program combines the reflected configurations with a rotation by π and adds or subtracts the paired configurations as necessary for g or u. Note that NFCN and NCON are set for the total number of functions and configurations. NHUG = +2 is the tag which instructs the program to perform the rotation and block diagonalize the total secular equation taking only the g block.

The energies in this case are:

1. Total electronic energy = -1.791067 au
2. Electronic + nuclear (potential curve) = -1.076781 au
3. Dissociation energy = -.076781 au

Note that although the same functions were used in both H_2 calculations, the one with symmetrized orbitals has a slightly lower. energy. This is because the symmetrized orbitals allow two linear coefficients, while in the total molecular inversion option there is only one. The total inversion, in effect, gives $C_1'(\sigma\sigma+\sigma'\sigma') = C_1(\sigma_g\sigma_g+\sigma_u\sigma_u)$, and we see that $C_1 = \sqrt{2}/2$. However, the total inversion requires only 3/2 to 3/4 the work required by the symmetrized orbitals, and if only $\sigma_g\sigma_g$ were used in the symmetrized case, a poorer answer would result.

The $C_1\sigma_g\sigma_g + C_2\sigma_u\sigma_u$ calculation can be improved by varying the parameters of the σ_u orbitals, since they are not restricted to be equal to the parameters of the σ_g orbitals as is the case of total inversion. They were set equal purely to demonstrate the relative effect of the two options.

Some specific hints are also helpful for actual use of the program on particular computers.

On machines having some type of CHAINing feature, the programs themselves can be overlaid. For example, the IBM 7094/7044 DCOS IBSYS monitor, version 13, was used with three links. The INTEGRAL, MATRIX, and SEARCH branches were included in one link for optimum efficiency, and the SETUP and OUTPUT branches formed the other two links.

An additional space-speed saving can be effected in systems with adjustable input-output buffer sizes, such as the Honeywell Automath 800/1800 monitor, by buffering the two-electron integral tape to the smallest possible size, since only two words are written per logical record; and by buffering the spin-permutation tape to the smallest size which will include N + ND×ND words in one logical record. Tapes KW and KR should be buffered with the largest double buffers possible, since tape handling by subroutine INTEG is the time-controlling factor.

On the Honeywell 800/1800 system, a small calling program is necessary to set up the monitor for use with variable tape identifiers. The entire deck setup is as follows:

```
*JOBID,JOBNAME,IO∅2∅3∅5,∅8SN∅∅25,∅9DB∅∅19,∅6DB∅2∅∅,∅7DB∅2∅∅
*  Project number xxx, users name, any special instructions to
*  be typed at console for operator.  (64 columns/card)

 TITLEMOLEC
     CALL DIAT
     I=0
     WRITE(6)I
     WRITE(7)I
     WRITE(8)I
     WRITE(9)I
     END
 TITLEDIAT --- entire diatomic program deck as presented in App. IV
*DATA
  6  7  8  9  3  5  (Tape identifiers, corresponding to *JOBID card
                     above)
-Remainder of input deck-
999
*ENDFILE
```

On the other hand, when the IBM 7094/7044 DCOS system is used, the monitor sets up all buffers when variable tape names are used, and

rather than tricking the monitor with the four statements WRITE(n)I above, one must use a MAP program which deletes the unused buffers. Copies of this program are available on request, or the following logic may be used to create the program for a specific installation. To delete the buffer for peripheral unit nu, the MAP program is

```
$IBMAP BUF.     NODECK
       ENTRY    .UNnn.
.UNnn. PZE
       END
```

The ENTRY and PZE instructions are repeated with different numbers Ø1, Ø2, ... as desired to delete any unnecessary unit.

The format for control cards, accounting cards, etc. can be found by consulting the appropriate IBM manuals and the notices published by the particular installation.

In the program listings (App. IV) the reader will note several comment cards relevant to particular machines, and accompanying FORTRAN statements. These must be included or pulled as necessary. The comments are considered self-explanatory.

The NO^+ Calculation

As an illustration of the use of the spin-permutation program options, the following sample calculation on NO^+ is presented. The approximations used were picked more to illustrate the use of the program than for their physical validity and thus the calculation is by no means a definitive one.

To do a complete 14 electron spin problem, 14! 429x429 matrices U(P) would be required, which is patently impossible. The approxi-

mations used to reduce this number to a manageable one are:

1. The closing of the shells which include the ten inner electrons so that the spatial configuration is approximately represented by

   $$\pi 2p_{+N}\pi 2p_{+O}\pi 2p_{-N}\pi 2p_{-O}(\sigma 1s)_N^2\ (\sigma 1s)_O^2\ (\sigma 2s)_N^2\ (\sigma 2s)_O^2\ (\sigma 2p_\sigma)_{ON}^2$$

   and thus requires only two spin functions

   $$\theta^4_{001}[1/\sqrt{2}(\alpha\beta-\beta\alpha)]^5 \text{ and } \theta^4_{002}[1/\sqrt{2}(\alpha\beta-\beta\alpha)]^5 .$$

2. Orthogonalization of the closed shell (doubly occupied) orbitals. This results in a spatial configuration of seven shells of two-electron pairs which are pairwise orthogonal.

With the open shell electrons listed first, the auxiliary permutation vector for the identity permutation is

$$1\ 2\ 3\ 4\ 55\ 66\ 77\ 88\ 99$$

and obviously no permutations are necessary between electrons 55, 66, etc. which reduces the number of permutations necessary for spin reasons to $14!/2^5$. We now take advantage of the spatial orthogonalities which were purposely introduced.

As pointed out in App. I, any permutation which produces three or more integrals $(i|j)$ which are zero can be eliminated, since it cannot contribute to the secular equation. Inspection of the auxiliary permutation vector above shows that only 20 permutations among the first four orbitals can contribute to the secular equation, and that no more than one interchange of the closed shell functions is allowed at a time.

Thus, there are 31 allowed interchanges of the closed shell orbitals with themselves or with the open shell orbitals 1-4.

The twenty allowed permutations of the open shell set result in 620 permutations which can contribute to the secular equation within this particular closed shell and orthogonality system, and the result is 620 2×2 matrices U(P) which is obviously a considerable improvement over the complete open shell treatment.

To make the input deck slightly easier to prepare, the orthogonalities in the set of four open shell electrons are ignored, and all 4! permutations among them are produced in the program. Hence there are $31 \times 4! = 744$ permutations and their corresponding U(P) produced.

The input deck for this calculation is shown in Table 11. Note that the paired orbitals are replaced by their canonical numbers, and that IOSH = 4. Since the permutations among the ten closed shell electrons are explicitly done by hand, no auxiliary permutation vector is needed in the input deck. The tape identifiers and quadrature points have been omitted. Preparation of the spin tape required about two hours on the Honeywell 800 and about eight minutes on an IBM 7094/7044 direct coupled system.

Once the spin tape was prepared, the NO^+ calculation itself took about three minutes on the 7094 and about twenty minutes on the H-800. The resulting energy was -105.93 au, which is of the right order of magnitude, but does not even show binding over the separated atom calculations of Clementi (1964). Due to limited time available

TABLE 10

SAMPLE INPUT DECK

```
*DATA
  6   7   8   9   3   5
            32                                                   GAUSSIAN
        .190783685503E 01 .174753079771E 01 .161383070701E 01 .150164963465E 01
        .140711169265E 01 .132722816436E 01 .125967131766E 01 .120261380877E 01
        .115461300423E 01 .111452664241E 01 .108145075383E 01 .105467367377E 01
        .103364190379E 01 .101793486429E 01 .100724637642E 01 .100136994325E 01
        .730957239412E 03 .139000007231E 03 .567573218103E 02 .307248338223E 02
        .192903384927E 02 .132773572106E 02 .973159274421E 01 .746776126583E 01
        .593549776333E 01 .485102216521E 01 .405597167027E 01 .345632836893E 01
        .299342316015E 01 .262911367674E 01 .233773752605E 01 .210151950149E 01
        .000000000000E-80 .000000000000E-80 .000000000000E-80 .000000000000E-80
        .000000000000E-80 .000000000000E-80 .000000000000E-80 .000000000000E-80
        .257983042030E 00 .266649570536E 00 .275984138460E 00 .286203763088E 00
        .297570455864E 00 .310412608788E 00 .325157698614E 00 .342384529758E 00
        .362910948974E 00 .387950049687E 00 .419409197727E 00 .460517871740E 00
        .517319815321E 00 .602908470418E 00 .753376991183E 00 .113289624202E 01
        .592394427105E-01 .902087498271E-01 .112694165954E 00 .130977494017E 00
        .146545764546E 00 .160138998352E 00 .172206801722E 00 .183062928959E 00
        .192949871710E 00 .202069518183E 00 .210599104372E 00 .218700280051E 00
        .226524883669E 00 .234219238443E 00 .241927970606E 00 .249797978606E 00
        .000000000000E-80 .000000000000E-80 .000000000000E-80 .000000000000E-80
        .000000000000E-80 .000000000000E-80 .000000000000E-80 .000000000000E-80
    4   6   1   2   4   1
  12    10     6     9     5     3
  .5773502692  -.2886751346  -.2886751346  -.2886751346  -.2886751346
  .5773502692
  .0000000000   .5000000000  -.5000000000  -.5000000000   .5000000000
  .0000000000
 1.         1  2   3   4
 LIH TEST RUN
 3.         1.          1.5
 4  0  1  4
   1 2.44       2.53
   2 1.60       1.45
   3  .92      - .90
   4  .64      - .32          1
 1  1  2  3  4
    2  2  1  1  2  1
   1    2
.7071067812   -.7071067812
 1.0       1  2
 H2 GROUND STATE TEST RUN NO. 1                       -1.
  1.        1.          1.4
 2  1  2  4
   1 1.06       .65
   2  .65       .67
   3 1.06       .65                  1
   4  .65       .67                  1
 1  1  2
 2  3  4
 1  2  2  1  1  2  1
 H2 GROUND STATE TEST RUN NO. 2                       -1.
  1.        1.          1.4
 2  2  2  4
   1 1.06       .65
   2  .65       .67
   3 1.06      -.65
   4  .65      -.67
 1  1  2
 2  3  4
999
*ENDFILE
```

TABLE 11

INPUT DECK FOR NO^+ CALCULATION

```
*DATA
    14192001002004031
 3413 3414 3417 3418 3429 3430 3433 3434 3477 3478 3481 3482 3493 3494
 3497 3498 3669 3670 3673 3674 3685 3686 3689 3690 3733 3734 3737 3738
 3749 3750 3753 3754 5461 5462 5465 5466 5477 5478 5481 5482 5525 5526
 5529 5530 5541 5542 5545 5546 5717 5718 5721 5722 5733 5734 5737 5738
 5781 5782 5785 5786 5797 5798 5801 5802 6485 6486 6489 6490 6501 6502
 6505 6506 6549 6550 6553 6554 6565 6566 6569 6570 6741 6742 6745 6746
 6757 6758 6761 6762 6805 6806 6809 6810 6821 6822 6825 6826 9557 9558
 9561 9562 9573 9574 9577 9578 9621 9622 9625 9626 9637 9638 9641 9642
 9813 9814 9817 9818 9829 9830 9833 9834 9877 9878 9881 9882 9893 9894
 9897 989810581105821058510586105971059810601106021064510646106491065O
1066110662106651066610837108381084110842108531085410857108581090110902
1090510906109171091810921109221262912630126331365812645126461264912650
1269312694126971269812709127101271312714128851288612889128901290112902
1290512906129491295012953129541296512966129691297O
    .1020622220  -.1020622220  -.1020622220   .1020622220  -.1020622220
    .1020622220   .1020622220  -.1020622220  -.1020622220   .1020622220
    .1020622220  -.1020622220   .1020622220  -.1020622220  -.1020622220
    .1020622220  -.1020622220   .1020622220   .1020622220  -.1020622220
    .1020622220  -.1020622220  -.1020622220   .1020622220   .1020622220
   -.1020622220  -.1020622220   .1020622220  -.1020622220   .1020622220
    .1020622220  -.1020622220  -.0510311100   .0510311100   .0510311100
   -.0510311100   .0510311100  -.0510311100  -.0510311100   .0510311100
    .0510311100  -.0510311100  -.0510311100   .0510311100  -.0510311100
    .0510311100   .0510311100  -.0510311100   .0510311100  -.0510311100
   -.0510311100   .0510311100  -.0510311100   .0510311100   .0510311100
   -.0510311100  -.0510311100   .0510311100   .0510311100  -.0510311100
    .0510311100  -.0510311100  -.0510311100   .0510311100  -.0510311100
    .0510311100   .0510311100  -.0510311100   .0510311100  -.0510311100
   -.0510311100   .0510311100   .0510311100  -.0510311100  -.0510311100
    .0510311100  -.0510311100   .0510311100   .0510311100  -.0510311100
    .0510311100  -.0510311100  -.0510311100   .0510311100  -.0510311100
    .0510311100   .0510311100  -.0510311100  -.0510311100   .0510311100
    .0510311100  -.0510311100   .0510311100  -.0510311100  -.0510311100
    .0510311100  -.0510311100   .0510311100   .0510311100  -.0510311100
    .0510311100  -.0510311100  -.0510311100   .0510311100   .0510311100
   -.0510311100  -.0510311100   .0510311100  -.0510311100   .0510311100
    .0510311100  -.0510311100   .0510311100  -.0510311100  -.0510311100
    .0510311100  -.0510311100   .0510311100   .0510311100  -.0510311100
   -.0510311100   .0510311100   .0510311100  -.0510311100   .0510311100
   -.0510311100  -.0510311100   .0510311100  -.0510311100   .0510311100
    .0510311100  -.0510311100   .0510311100  -.0510311100  -.0510311100
    .0510311100   .0510311100  -.0510311100  -.0510311100   .0510311100
   -.0510311100   .0510311100   .0510311100  -.0510311100   .0510311100
   -.0510311100  -.0510311100   .0510311100  -.0510311100   .0510311100
    .0510311100  -.0510311100  -.0510311100   .0510311100   .0510311100
   -.0510311100   .0510311100  -.0510311100  -.0510311100   .0510311100
    .1020622220  -.1020622220  -.1020622220   .1020622220  -.1020622220
    .1020622220   .1020622220  -.1020622220  -.1020622220   .1020622220
    .1020622220  -.1020622220   .1020622220  -.1020622220  -.1020622220
    .1020622220  -.1020622220   .1020622220   .1020622220  -.1020622220
    .1020622220  -.1020622220  -.1020622220   .1020622220   .1020622220
   -.1020622220  -.1020622220   .1020622220  -.1020622220   .1020622220
    .1020622220  -.1020622220
    .0000000000   .0000000000   .0000000000   .0000000000   .0000000000
    .0000000000   .0000000000   .0000000000   .0000000000   .0000000000
    .0000000000   .0000000000   .0000000000   .0000000000   .0000000000
    .0000000000   .0000000000   .0000000000   .0000000000   .0000000000
    .0000000000   .0000000000   .0000000000   .0000000000   .0000000000
    .0000000000   .0000000000   .0000000000   .0000000000   .0000000000
    .0000000000   .0000000000   .0883883470  -.0883883470  -.0883883470
    .0883883470  -.0883883470   .0883883470   .0883883470  -.0883883470
   -.0883883470   .0883883470   .0883883470  -.0883883470   .0883883470
   -.0883883470  -.0883883470   .0883883470  -.0883883470   .0883883470
    .0883883470  -.0883883470   .0883883470  -.0883883470  -.0883883470
    .0883883470   .0883883470  -.0883883470  -.0883883470   .0883883470
   -.0883883470   .0883883470   .0883883470  -.0883883470  -.0883883470
    .0883883470   .0883883470  -.0883883470   .0883883470  -.0883883470
   -.0883883470   .0883883470   .0883883470  -.0883883470  -.0883883470
```

```
 .0883883470  -.0883883470   .0883883470   .0883883470  -.0883883470
 .0883883470  -.0883883470  -.0883883470   .0883883470  -.0883883470
 .0883883470   .0883883470  -.0883883470  -.0883883470   .0883883470
 .0883883470  -.0883883470   .0883883470  -.0883883470  -.0883883470
 .0883883470  -.0883883470   .0883883470   .0883883470  -.0883883470
 .0883883470  -.0883883470  -.0883883470   .0883883470   .0883883470
-.0883883470  -.0883883470   .0883883470  -.0883883470   .0883883470
 .0883883470  -.0883883470   .0883883470  -.0883883470  -.0883883470
 .0883883470  -.0883883470   .0883883470   .0883883470  -.0883883470
-.0883883470   .0883883470   .0883883470  -.0883883470   .0883883470
-.0883883470  -.0883883470   .0883883470   .0883883470  -.0883883470
-.0883883470   .0883883470  -.0883883470   .0883883470   .0883883470
-.0883883470  -.0883883470   .0883883470   .0883883470  -.0883883470
 .0883883470  -.0883883470  -.0883883470   .0883883470  -.0883883470
 .0883883470   .0883883470  -.0883883470   .0883883470  -.0883883470
-.0883883470   .0883883470   .0883883470  -.0883883470  -.0883883470
 .0883883470  -.0883883470   .0883883470   .0883883470  -.0883883470
 .0000000000   .0000000000   .0000000000   .0000000000   .0000000000
 .0000000000   .0000000000   .0000000000   .0000000000   .0000000000
 .0000000000   .0000000000   .0000000000   .0000000000   .0000000000
 .0000000000   .0000000000   .0000000000   .0000000000   .0000000000
 .0000000000   .0000000000   .0000000000   .0000000000   .0000000000
 .0000000000   .0000000000   .0000000000   .0000000000   .0000000000
 .0000000000   .0000000000
 1.0         1  2  3  4  5  6  7  8  9 10 11 12 13 14
-1.0         1  2  3  4  5  7  6  8  9 10 11 12 13 14
-1.0         1  2  3  4  5  9  7  8  6 10 11 12 13 14
-1.0         1  2  3  4  5 11  7  8  9 10  6 12 13 14
-1.0         1  2  3  4  5 13  7  8  9 10 11 12  6 14
-1.0         1  2  3  4  5  6  7  9  8 10 11 12 13 14
-1.0         1  2  3  4  5  6  7 11  9 10  8 12 13 14
-1.0         1  2  3  4  5  6  7 13  9 10 11 12  8 14
-1.0         1  2  3  4  5  6  7  8  9 11 10 12 13 14
-1.0         1  2  3  4  5  6  7  8  9 13 11 12 10 14
-1.0         1  2  3  4  5  6  7  8  9 10 11 13 12 14
 1.          2  3  4  5  1  6  7  8  9 10 11 12 13 14
 1.          2  3  4  7  5  6  1  8  9 10 11 12 13 14
 1.          2  3  4  9  5  6  7  8  1 10 11 12 13 14
 1.          2  3  4 11  5  6  7  8  9 10  1 12 13 14
 1.          2  3  4 13  5  6  7  8  9 10 11 12  1 14
-1.0         1  3  4  5  2  6  7  8  9 10 11 12 13 14
-1.0         1  3  4  7  5  6  2  8  9 10 11 12 13 14
-1.0         1  3  4  9  5  6  7  8  2 10 11 12 13 14
-1.0         1  3  4 11  5  6  7  8  9 10  2 12 13 14
-1.0         1  3  4 13  5  6  7  8  9 10 11 12  2 14
 1.          1  2  4  5  3  6  7  8  9 10 11 12 13 14
 1.          1  2  4  7  5  6  3  8  9 10 11 12 13 14
 1.          1  2  4  9  5  6  7  8  3 10 11 12 13 14
 1.          1  2  4 11  5  6  7  8  9 10  3 12 13 14
 1.          1  2  4 13  5  6  7  8  9 10 11 12  3 14
-1.0         1  2  3  5  4  6  7  8  9 10 11 12 13 14
-1.0         1  2  3  7  5  6  4  8  9 10 11 12 13 14
-1.0         1  2  3  9  5  6  7  8  4 10 11 12 13 14
-1.0         1  2  3 11  5  6  7  8  9 10  4 12 13 14
-1.0         1  2  3 13  5  6  7  8  9 10 11 12  4 14
   NO+ TRIAL CALC.
   8.        7.          2.0
 14  0  1  9  0  0  0  1
    1 3.268       -1.         0  0  1
    2 3.685        1.         0  0  1
    3 1.52        -.8         0  0 -1
    4 1.66         .8         0  0 -1
    5 3.827575     .2
    6 8.132053    8.027197
    7 7.144851 -6.981715
    8 4.6555      .477334      1
    9 3.031213 -4.54682       0  1
  1  1  2  3  4  5  5  6  6  7  7  8  8  9  9
999
*ENDFILE
```

to the author, no attempt was made to improve this calculation by variation of the non-linear parameters or by making more realistic physical approximations. Upon completion of the single one-shot run it was decided that the original purpose of this study had been achieved, that of demonstrating that a calculation on a large many-electron diatomic molecule is possible and practical with the present modification of the diatomic program.

The short time required for the actual calculation shows that parameter variation and even some configuration mixing are possible in reasonable amounts of computer time, and a much improved energy obtainable even with the limited spin set used.

APPENDIX IV

LISTING OF DIATOMIC PROGRAM

```
**    ****    ****    ****    ****    ****    ****    ****    ****    ****    **
 TITLEDIAT                                                               DIA
C                                                                        DIA
C   REVISED DIATOMIC MOLECULE PROGRAM                                    DIA
C                                                                        DIA
C       REV. DATE  6/16/66                                               DIA
C                                                                        DIA
C    DATA INPUT AND CONTROL LINK                                         DIA
C    INPUT DEFINITIONS                                                   DIA
C      ZA - CHARGE ON ATOM A                                             DIA
C      ZB - CHARGE ON ATOM B                                             DIA
C      RMAX - INTERNUCLEAR SEPARATION                                    DIA
C      STEP3 - INITIAL STEP SIZE FOR PARAMETER SEARCH                    DIA
C      STEP2 - FINAL TOLERANCE                                           DIA
C      RMIN - MINIMUM INTERNUCLEAR SEPARATION                            DIA
C      RSTEP - DECREMENT TO R    UNTIL REACHES RMIN                      DIA
C      N - NO. OF ELECTRONS                                              DIA
C      NHUG - HET-HOMO.GERADE-UNGERADE TAG.(0=HET.,-=UNG.,+=GER.)        DIA
C      NCON - NO. OF SPATIAL CONFIGURATIONS                              DIA
C      NFCN - NO. OF ONE-ELECTRON SPATIAL ORBITALS                       DIA
C      NPC - NO. OF FUNCTIONS(ORBITALS) TO BE VARIED(PARAM. SRCH)        DIA
C      NE- DESIRED ROOT OF SEC. EQN.(0=GND.STATE, 1=1ST EXCITED ST.,ETC)DIA
C      LSRCH - LINEAR VS. STEEPEST DESCENT PARAM SRC(,0= GRAD,+=LIN.)    DIA
C      NOTRF - TRANSFORMATION TAG. SEE SUBROUTINE TXFORM                 DIA
C      NU - NUMBER OF FUNCTIONS TO BE PROJECTED OUT IF NOTRF=1  PARAM    DIA
C      SEARCH STARTS ON NU + 1 ST FUNCTION                               DIA
```

```
C       KSIM - (ITAG(4))  SIMULTANEOUS VARIATION TAG. IF NON-ZERO, VARIES
C       MO-TH AND NFCN/2+MO-TH FUNCTIONS SIMULTANEOUSLY
C       IS - IF =2 , TAPE KR IS MOUNTED FROM PREVIOUS RUN, AND PROG.
C       SETS ITX=2
C     FUNCTION CARDS ---------
C     DELTA(I)=FPAR(1,I) , ALPHA(I)=FPAR(2,I)
C     FPAR= WORKING SET OF DELTA,ALPHA
C     FPARO= BEST SET DETERMINED SO FAR
C     NFPAR= FIXED EXPONENTS
C     N(I)=NFPAR(1,I),M(I)=NFPAR(2,I),NU(I)=NFPAR(3,I),PARITY(I)=
C     NFPAR(4,I)(1=U,0=G),NFPAR(5,I)-NOT USED,NFPAR(6,I)-VARIATION TAG
C     0=VARY DELT AND ALF,1=VARY ALF ONLY,2=VARY DELT ONLY,3=SKIP BOTH
C     CONFIGURATION CARDS ARE READ BY SUBROUTINE CONFIG
C
C    DIMENSION OF H1,S1,H2 BASED ON 16 FUNCTIONS (NFCN=16)
C
      COMMON/SPACE/ZA,ZB,R,N,NHUG,NCON,MULT,KW,KR,KOR,NT,JNT,JCODE,
     1NPERMS,ND,NFCN,MMAT,N10,NMAT,NE,NPC,LSPARE,MSPARE,ITX,N1,NC1,NC2P,
     2LSRCH,JKW3,LIAR,STEP1,STEP2,E0,N0,M0,IS,A1,A2,EFIN,SAVEA(9),MAD(2)
     3 ,FPARO(2,16),FPAR(2,16),NFPAR(6,16),ITAG( 6),ICTAG(64),
     4DELT(25),RMAX,RMIN,RSTEP,STEP3
      COMMON/DATBLS/D1(11,11),DD1(36,7),DD2(43,7),JMAX,WTINF,POINT(40),
     1WT(40),NMINUS,RULE(2)
      COMMON/WORK/NEL,NISP,MULT1,ND1,IOSH,JGEN,IDEN(3),KW1,KR1,NT1,KOR1,
     1DA(2917)    , S1(9588)
      COMMON/CIJ/C(16,16),NOTRF,NU,MU,KRUD(9)
      EQUIVALENCE(KR1,I),(KOR1,J) ,(IO,LSPARE)
      EQUIVALENCE (ITAG(1),IN),(ITAG(2),KINT)
      EQUIVALENCE (NPCH,ITAG(3))
      COMMON LCON (150)
  100 FORMAT(12I3)
  101 FORMAT(8A6,3F10.6)
  102 FORMAT(7F10.4)
  103 FORMAT(I5,2F10.6,6I3)
  104 FORMAT(1H020X,15HSEC EQN TOO BIGI6)
```

```
  105 FORMAT(1H020X,15HWRONG PERM TAPE2I6)
  111 FORMAT(8E10.5)
C
C   HONEYWELL
      IN=2
C   FOR  IBM  SET  IN = 5
      MSPARE=42
      ITX=1313
      LIAR=0
C
   26 CALL SETUP(IN)
   25 REWIND NT
      REWIND KW
      REWIND KR
      READ(IN,101) (SAVEA(I),I=1,8), A1,A2,EFIN
      READ(IN,102) ZA,ZB,RMAX,STEP3,STEP2,RMIN,RSTEP
      IF(RMIN.EQ.0.)RMIN=RMAX
      READ(IN,100) N,NHUG,NCON,NFCN,NPC,NE,LSRCH,NOTRF,NU,ITAG(4) ,IS
      IF(IS.EQ.0) IS=1
      DO 3 N10=1,NFCN
      READ(IN,103) N1,FPARO(1,N1),FPARO(2,N1),(NFPAR(JNT,N1),JNT=1,6)
      MO=N1
      IF(ABS(FPARO(2,MO)).GT.1.2*FPARO(1,MO)) FPARO(2,MO)=SIGN(1.2*
     *FPARO(1,MO),FPARO(2,MO))
      FPAR(1,N1)=FPARO(1,N1)
      FPAR(2,N1)=FPARO(2,N1)
    3 CONTINUE
      CALL CONFIG (1,LCON ,N,NCON,IN,IO)
      JCODE=1000*N+10*IOSH+MULT
      IF(NOTRF.GE.0) GO TO 9
   49 DO 48 I=1,N
   48 READ(IN,111) (C(I,J),J=1,N)
    9 REWIND NT
      READ(NT) IDEN
      IF(JCODE.NE.IDEN(3)) GO TO 8
```

```
      REWIND NT
      ND=IDEN(1)
      MMAT=NFCN*(NFCN+1)/2
      NMAT=NCON*ND
      IF(NMAT.GT.MSPARE) GO TO 10
      IF(NPC.NE.0) NPC=NPC+NU
      IF(IABS(NHUG).EQ.2) ITAG(4)=1
    5 R=RMAX
      MO = 1 + NU
      NO=1
      ITX=1
      IF(IS.EQ.2) ITX=2
      STEP1 = STEP3
   11 CALL HDG
      CALL CONFIG (2,LCON ,N,NCON,IN,IO)
    7 CALL INTEG
      CALL MATRIX( IN,LCON ,NCON,N)
      CALL SEARCH
      IF(ITX.NE.0) GO TO 7
      CALL OUTPUT (LCON ,NCON,N)
      IF(RMAX.LE.RMIN) GO TO 1
      RMAX=RMAX-RSTEP
      R=RMAX/R
      DO 22 I=1,2
      DO 22 J=1,16
      FPARO(I,J)=FPARO(I,J)*R
   22 FPAR(I,J)=FPARO(I,J)
      GO TO 5
    8 WRITE(IO,105) JCODE, IDEN(3)
      CALL EXIT
   10 WRITE(IO,104) NMAT
      CALL EXIT
    1 CALL SSWTCH(4,MORE)
      IF(MORE.NE.1) GO TO 222
      REWIND NPCH
```

```
      WRITE(NPCH,101) (SAVEA(I),I=1,8),A1,A2,EFIN                      DIA 1310
      WRITE(NPCH,102)ZA,ZB,R,STEP3,STEP2,RMIN,RSTEP                    DIA 1320
      MU=NFCN-MO -1                                                    DIA 1330
      WRITE(NPCH,100) N,NHUG,NCON,NFCN,MU,NE,LSRCH,NOTRF,MO            DIA 1340
      DO 333 N1=1,NFCN                                                 DIA 1350
  333 WRITE(NPCH,103) N1,FPARO(1,N1),FPARO(2,N1),(NFPAR(JNT,N1),JNT=1,6)DIA 1360
      CALL CONFIG(3,LCON ,N,NCON,IN,NPCH)                              DIA 1370
      ENDFILE NPCH                                                     DIA 1380
  222 READ(IN,100) JNT,NEL,NISP,MULT,ND,IOSH,JGEN                      DIA 1390
      IF(JNT.EQ.999) CALL EXIT                                         DIA 1400
C                                                                      DIA 1410
C      HONEYWELL 800 ONLY   -  FOR SOME REASON THIS PREVENTS UNDEFINED DIA 1420
C     TAPE POSITION ERRORS WHEN STARTING A NEW CALCULATION.            DIA 1430
C                                                                      DIA 1440
      KW=6                                                             DIA 1450
      KR=7                                                             DIA 1460
C                                                                      DIA 1470
C                                                                      DIA 1480
      IF(JNT.NE.0) GO TO 25                                            DIA 1490
      GO TO 26                                                         DIA 1500
      END                                                              DIA 1510

**    ****    ****    ****    ****    ****    ****    ****    ****    ****      **
      SUBROUTINE HDG                                                   HDG   10
C      PRINTS HEADING LINES IN OUTPUT                                  HDG   20
      COMMON/SPACE/ZA,ZB,R,N,NHUG,NCON,MULT,KW,KR,KOR,NT,JNT,JCODE,    HDG   30
     1NPERMS,ND,NFCN,MMAT,N10,NMAT,NE,NPC,LSPARE,MSPARE,ITX,N1,NC1,NC2P,HDG   40
     2LSRCH,JKW3,LIAR,STEP1,STEP2,EO,NO,MO,IS,A1,A2,EFIN,SAVEA(9),MAD(2)HDG   50
     3 ,FPARO(2,16),FPAR(2,16),NFPAR(6,16),ITAG(16),ICTAG(6),LCON(6,8), HDG   60
     4DELT(25),RMAX,RMIN,RSTEP,STEP3                                   HDG   70
      COMMON/DATBLS/D1(11,11),DD1(36,7),DD2(43,7),JMAX,WTINF,POINT(40), HDG   80
     1WT(40),NMINUS,RULE(2)                                            HDG   90
      EQUIVALENCE(I,JNT),(TUP,NC2P)                                    HDG  100
      EQUIVALENCE (IO,LSPARE)                                          HDG  110
      EQUIVALENCE (BLANK,ICTAG)                                        HDG  120
      DIMENSION HAG(8),BLANK(3)                                        HDG  130
  999 DATA(HAG(I),I=1,8)/5HHETER,5H  HOM,5HONUC.,5H GER ,5H UNG  ,6HMOL.HDG  140
```

```
     * I,6HNVERTD,6H       /                                              HDG
  10 FORMAT(15X,12HCJT W SSWTCH  /)                                       HDG
 303 FORMAT(1H18A6//7X,3HZA=F8.2,3X,3HZB=F8.2,3X,2HN=I2,3X,5H2S+1=I2,3XHDG
     *,2HC=I2,3X,2HR=F8.3,4H(AU)3X,2HR=F8.4,5H(ANG)  /)                   HDG
      TUP= .52917*R                                                       HDG
      WRITE(IO,303)(SAVEA(I),I=1,8),ZA,ZB,N,MULT,NCON,R,TUP               HDG
 100 FORMAT(15X,3A5,2A6  /)                                               HDG
      IF(NHUG.EQ.0) GO TO 2                                               HDG
      BLANK(1)=HAG(8)                                                     HDG
      BLANK(2)=HAG(8)                                                     HDG
      IF(IABS(NHUG).NE.2) GO TO 3                                         HDG
      BLANK(1)=HAG(6)                                                     HDG
      BLANK(2)=HAG(7)                                                     HDG
   3  BLANK(3)=HAG(4)                                                     HDG
      IF(NHUG.LT.0) BLANK(3)=HAG(5)                                       HDG
      WRITE(IO,100) HAG(2),HAG(3),BLANK(3),BLANK(1),BLANK(2)              HDG
      GO TO 7                                                             HDG
   2  WRITE(IO,100) HAG(1),HAG(3)                                         HDG
    7 CONTINUE                                                            HDG
      IF(LIAR.NE.0) WRITE(IO,10)                                          HDG
      WRITE(IO,107) RULE,JMAX                                             HDG
 107 FORMAT(1H0,20X,2A6,21HINTEGRATION, NO. PTS=  I4 /)                   HDG
    9 RETURN                                                              HDG
      END                                                                 HDG
```

```
      SUBROUTINE CONFIG( NRW,LCON,N,NCON,IN,IO)                         CON
C     READ OR PRINT CONFIG CARDS                                        CON
      DIMENSION LCON(NCON,N)                                            CON
  100 FORMAT(12I3)                                                      CON
  106 FORMAT(5X,4HCONF,I7,5X,3HFCN 2X,20I3)                             CON
      GO TO (1,2,3),NRW                                                 CON
    1 DO 4 N10= 1,NCON                                                  CON
      READ(IN,100) N1,(LCON(N1,JNT),JNT=1,N)                            CON
    4 CONTINUE                                                          CON
      RETURN                                                            CON
    2 DO 20 N1=1,NCON                                                   CON
   20 WRITE(IO,106)N1,(LCON(N1,J),J=1,N)                                CON
      RETURN                                                            CON
    3 DO 21 N1=1,NCON                                                   CON
   21 WRITE(IO,100)N1,(LCON(N1,J),J=1,N)                                CON
      RETURN                                                            CON
      END                                                               CON

**    ****    ****    ****    ****    ****    ****    ****    ****    ****    **
      SUBROUTINE SETUP (IN)                                             SET
C      CONTROLLING PROGRAM OF SETUP      BRANCH                         SET
C      SETS PERMANENT DATA BLOCK AND MAKES INITIAL SPIN TAPE            SET
      COMMON/SPACE/ZA,ZB,R,N,NHUG,NCON,MULT,KW,KR,KOR,NT,JNT,JCODE,     SET
     1NPERMS,ND,NFCN,MMAT,N10,NMAT,NE,NPC,LSPARE,MSPARE,ITX,N1,NC1,NC2P,SET
     2LSRCH,JKW3,LIAR,STEP1,STEP2,E0,NO,MO,IS,A1,A2,EFIN,SAVEA(9),MAD(2)SET
     3 ,FPARO(2,16),FPAR(2,16),NFPAR(6,16),ITAG(16),ICTAG(6),LCON(6,8), SET
     4DELT(25),RMAX,RMIN,RSTEP,STEP3                                    SET
      COMMON/WORK/NEL,NISP,MULT1,ND1,IOSH,JGEN,IDEN(3),KW1,KR1,NT1,KOR1,SET
     1DA(2917)    , S1(9588)                                            SET
      EQUIVALENCE (IOUT,LSPARE)                                         SET
      EQUIVALENCE (ITAG(2),KINT)    ,(ITAG(3),NPCH)                     SET
  100 FORMAT(12I3)                                                      SET
      IF(ITX.NE.1313) GO TO 1                                           SET
      READ(IN,100)  KW,KR,NT,KINT, IOUT,NPCH                            SET
      CALL TABLE(IN)                                                    SET
      READ(IN,100) JNT,NEL,NISP,MULT,ND,IOSH,JGEN                       SET
    1 IF(JNT.EQ.0) CALL SPIN (NT,NPERMS,IN,NEL,NISP,MULT,ND,IOSH,JGEN,  SET
```

```
      1IDEN,DA(1),DA(785),DA(857),DA(1577),DA(1600),DA(1650),S1)
       RETURN
       END

**     ****     ****     ****     ****     ****     ****     ****     ****     ****     **
       SUBROUTINE TABLE (M)
C     MAKES PERMANENT DATA BLOCK FOR INTEGRAL ROUTINES
       COMMON/DATBLS/D1(11,11),DD1(36,7),DD2(43,7),JMAX,WTINF,POINT(40),
      1WT(40),NMINUS,RULE(2)
       EQUIVALENCE (WT(1),I),(WT(2),J),(WT(3),K),(WT(4),A),(WT(5),B),
      *(WT(6),C)
C     APPENDIX II - EQN (64)
       DO 1 I=1,7
       DO 1 J=I,7
    1  DD1(I,J)=0.
       DD1(1,1)=1.
       DO 5 I=2,7
       A=2*I-1
    5  DD1(I,I)=DD1(I-1,I-1)*SQRT(A*(A-1.))
       DO 6 J=1,7
       K=J+1
       DO 6 I=K,36
       A=I+J-2
       B=2*I-1
       C=I-J
    6  DD1(I,J)=DD1(I-1,J)*SQRT(A/C*B/(B-2.))
C     APPENDIX II - EQN (65)
       DO 2 I=1,11
       DO 2 J=1,11
    2  D1(I,J)=0.
       D1(1,1)=1.
       DO 3 I=2,11
       A=I-1
       B=2*I-3
    3  D1(I,I)=D1(I-1,I-1)*A/B
       DO 4 J=1,9
       K=J+2
```

```
      DO 4 I=K,11,2
      A=I-1
      C=I-J
      B=I+J-1
    4 D1(I,J)=D1(I-2,J)*A/C*(A-1.)/B
C    APPENDIX II - EQN (66)
      DO12 I=1,43
      DO12 J=1,7
      A=I+J-1
      B=I-J+1
      C=4*I*I-1
   12 DD2(I,J)=A*B/C
      READ(M,100) JMAX,NMINUS,WTINF ,RULE
      READ(M,101) POINT
C    APPENDIX II - EQN (67)
      READ(M,101) WT
      RETURN
  100 FORMAT(6X,2I8,E30.12,2A6)
  101 FORMAT(6X,4E18.12  )
      END

**    ****    ****    ****    ****    ****    ****    ****    ****    ****     **
      SUBROUTINE SPIN (NT,NP,IN,N  ,NISP,MULT,ND,IOSH,JGEN,IDEN,UMAT,
     *ISP,ITE,ISSPM,JPRI,I1,USET)
C   MAKES PERM TAPE OF UMAT AND IPER WITH OPTIONS RANGING FROM CLOSED
C   SHELL TO COMPLETE OPEN SHELL
C
C   SPACE AND DIMENSIONS ARE SUFFICIENT FOR HANDLING THE  FULL
C   EIGHT ELECTRON PROBLEM
C
C    INPUT
C     NEL - NUMBER OF ELECTRONS
C     NISP - NUMBER OF SIMPLE SPIN PRODUCT FUNCTIONS (AABBA...)
C     MULT - MULTIPLICITY (2S+1)
C     ND - DEGENERACY (FNS OF KOTANI)
C      IOSH - NUMBER OF ELECTRONS TO BE INCLUDED IN PERM. SCAN
C     JGEN - NUMBER OF HAND GENERATED PERMUTATIONS
```

```
C       ( PERMS WHICH PRODUCE ZEROS DUE TO CLOSING OF SHELLS OR SPATIAL
C      ORTHOGONALITIES ARE OMITTED BY PROPER PREPARATION OF JGEN LIST
C
C    INPUT (CARDS)
C      ISP - ACTUAL CODING OF BIT CONFIGURATIONS FOR SPIN PRODUCT FUNCTIO
C      USET - COEFFICIENT MATRIX (DIMENSION NDXNISP)
C    JPRI  -    UNPAIRED TRUE PERMUTATION VECTOR
C    KPRI   -     AUXILIARY  PERM VECTOR WITH PAIRS INDICATED
C
C    OUTPUT       - ON TAPE NT
C       UMAT=ANTISYMMETRIZED MATRIX REPRESENTATION OF PERMUTATIONS
C      IPER - THE ACTUAL PERMUTATIONS (PERMUTED FUNCTION NUMBERS)
C      NP - THE NUMBER OF SETS (UMAT,IPER) WRITTEN ON TAPE NT
C
      DIMENSION IDEN(3),UMAT(ND,ND),ISP(NISP),ITE(NISP,N),ISSPM(N),
     *JPRI(N),I1(N),USET(ND,NISP),KPRI(20)
  100 FORMAT(14I5)
  101 FORMAT(5F14.10)
  102 FORMAT(F9.2,21I3)
      REWIND NT
      DO110 I=1,ND
      DO 9 J=1,ND
    9 UMAT(I,J)=0.
  110 UMAT(I,I)=1.
      NP=0
      LOCA=0
      READ(IN,100) (ISP(I),I=1,NISP)
C    UNPACK ISP INTO ITE
      DO 11 I=1,NISP
      IX = ISP(I)
      IZ = 2**(N-1)
      DO 11 J=1,N
      ITE(I,J)=IX/IZ
      IX=IX-IZ*ITE(I,J)
   11 IZ = IZ/2
```

```
      DO812 I=1,ND
      READ(IN,101) (USET(I,J),J=1,NISP)
  812 USET(I,NISP+1)=0.
      IDEN(1)=ND
      IDEN(2) = N
      IDEN(3)= 1000*N  +10*IOSH+MULT
      WRITE(NT) IDEN
      J1PER = 1
   20 READ(IN,102)  SIG, (JPRI(K), K=1,N) ,(KPRI(K),K=1,N)
      IF(KPRI(1).NE.0) GO TO 999
      DO 998 K=1,N
  998 KPRI(K)=JPRI(K)
  999 IF (NP.EQ.0) GO TO 27
      GO TO 116
   21 K1=IOSH-1
      DO 301 K=1,K1
      IF(KPRI(K+1).GT.KPRI(K)) GO TO 302
  301 CONTINUE
      IF(J1PER.GE.JGEN) GO TO 117
      J1PER = J1PER + 1
      GO TO 20
  302 DO 303 L=1,K
      ISSPM(L)=KPRI(L)
  303 I1(L)= JPRI(L)
      DO 304 L=1,K
      K1 = K-L+1
      KPRI(L)=ISSPM(K1)
  304 JPRI(L) = I1(K1)
      DO 305 L=1,K
      IF(ISSPM(L).LT.KPRI(K+1)) GO TO 306
  305 CONTINUE
  306 K1 = K-L+1
      JPRI(K1) = JPRI(K+1)
      JPRI(K+1) = I1(L)
      KPRI(K1) = KPRI(K+1)
```

```
      KPRI(K+1)= ISSPM(L)
      IF(MOD(K,4).LT.2) SIG=-SIG
  116 DO 10 I=1,NISP
   10 ISSPM(I)=0
      DO 14 I=1,NISP
      IX = 0
      DO 12 K=1,N
      IX = 2*IX
      I3=JPRI(K)
   12 IX = IX + ITE(I,I3)
      DO 13 K=1,NISP
      IF(IX.NE.ISP(K)) GO TO 13
      ISSPM(K)=I
      GO TO 14
   13 CONTINUE
   14 CONTINUE
      DO 1180 I=1,ND
      DO 1180 L=1,ND
      UTEM=0
      DO 1175 J = 1,NISP
      K=ISSPM(J)
      IF(K.EQ.0) GO TO 1175
      UTEM=UTEM+USET(I,J)*USET(L,K)
 1175 CONTINUE
 1180 UMAT(I,L)  =   UTEM*SIG
   27 WRITE(NT) (JPRI(I),I=1,N),((UMAT(K,J),K=1,ND),J=1,ND)
      NP = NP+1
      GO TO 21
  117 ENDFILE NT
      REWIND NT
      RETURN
      END
```

```
      SUBROUTINE INIEG
C
C      CONTROLLING PROGRAM OF INTEGRAL  BRANCH
C     GENERATES AND STORES ONE AND TWO ELECTRON INTEGRALS
C     KW= WRITE TAPE,  KR= READ TAPE WITH BEST SET OF INTEGRALS TO DATE
C      JTA AND JTB ARE COMPLETE INTEGRAL TABLES, WITH ALL DATA NECESSARY
C     FOR COMBINING TO MAKE THE TWO ELECTRON INTEGRALS./
C
C      SEE SUBROUTINE ONEL FOR TABLE LAYOUT OF (JTA(I,L),I=1,1460)
C     TOTAL INTEGRAL PACKAGE CONSISTS OF BANDI,GLIST, ONEL, TWOEL
C      COMBIN AND TAPE
C
      COMMON/SPACE/ZA,ZB,R,N,NHUG,NCON,MULT,KW,KR,KOR,NT,JNT,JCODE,
     1NPERMS,ND,NFCN,MMAT,N10,NMAT,NE,NPC,LSPARE,MSPARE,ITX,N1,NC1,NC2P,
     2LSRCH,JKW3,L1AR,STEP1,STEP2,E0,NO,MO,IS,A1,A2,EFIN,SAVEA(9),MAD(2)
     3 ,FPARO(2,16),FPAR(2,16),NFPAR(6,16),ITAG(16),ICTAG(6),LCON(6,8),
     4DELT(25),RMAX,RMIN,RSTEP,STEP3
      COMMON/WORK/JTB(1460,4),JTA(1460,4),I,J,L,L1,NTOT      ,DUMBO(289)
     1,S1(136),H1(136),REST(272)
      COMMON/DATBLS/D1(11,11),DD1(36,7),DD2(43,7),JMAX,WTINF,POINT(40),
     1WT(40),NMINUS,RULE(2)
      COMMON/CIJ/C(16,16),NOTRF,NU,MU,KRUD(9)
      EQUIVALENCE (LSPARE,IO)
      EQUIVALENCE (ITAG(2),KINT)
      EQUIVALENCE (JTA,ZG1),(JTB,H2)
      DIMENSION H2(9317), ZG1(1460,4)
      DATA FINAL/6HNOMORE/
C
  303 REWIND KW
      REWIND KINT
      REWIND NT
      REWIND KR
      NTOT=1
      L=0
      L1=0
```

```
      DO 302 I=1,NFCN                                                  INT  360
      DO 302 J=1,I                                                     INT  370
      L1=L1+1                                                          INT  380
      IX=NFCN/2                                                        INT  390
      IF(NOTRF.EQ.1) IX=IX+NU                                          INT  400
      IF((IABS(NHUG).EQ.2).AND.(J.GT.IX    )) GO TO 301                INT  410
      L=L+1                                                            INT  420
      IF(ITX.EQ.1) GO TO 309                                           INT  430
      IF(L.EQ.1) CALL TAPE(KR,1,JTA)                                   INT  440
      IF(JTA(11,L).EQ.L1) GO TO 309                                    INT  450
  358 WRITE(IO,399)L1,JTA(11,L),I,JTA(8,L),J,JTA(9,L)                  INT  460
      CALL EXIT                                                        INT  470
  309 CALL ONEL(I,J,JTA(1,L),JTA(1,L),JMAX)                            INT  480
      JTA(11,L)=L1                                                     INT  490
      S1(L1)=ZG1(17,L)                                                 INT  500
      IF(J.NE.I) GO TO 400                                             INT  510
      REST(I)=SQRT(S1(L1))                                             INT  520
      MERDE=IX+I                                                       INT  530
      IF(IABS(NHUG).EQ.2) REST(MERDE)=REST(I)                          INT  540
  400 H1(L1)=(2.*ZG1(10,L)-ZG1(18,L)/(2.*R))/R                         INT  550
      IF(L.LT.4) GO TO 302                                             INT  560
      CALL TAPE(KW,2,JTA)                                              INT  570
      L=0                                                              INT  580
      NTOT=NTOT+1                                                      INT  590
  301 CONTINUE                                                         INT  600
  302 CONTINUE                                                         INT  610
      L1=L+1                                                           INT  620
      DO 300 I=L1,4                                                    INT  630
      JTA(11,I)=0                                                      INT  640
  300 JTA(12,I)=20                                                     INT  650
      CALL TAPE(KW,2,JTA)                                              INT  660
      ENDFILE KW                                                       INT  670
      REWIND KW                                                        INT  680
      L1=0                                                             INT  690
C     NORMALIZE                                                        INT  700
```

```
      DO 304 I=1,NFCN
      DO 304 J=1,I
      L1=L1+1
      X=REST(I)*REST(J)
      S1(L1)=S1(L1)/X
      H1(L1)=H1(L1)/X
      IF(I.EQ.J) S1(L1)=1.
  304 CONTINUE
      I=L+4*(NTOT-1)
      I=I*(I+1)/2 +1
  310 CALL COMBIN(JTA,JTA,KINT,R,JMAX,REST)
      IF(NTOT.EQ.1) GO TO 241
      NTOT=NTOT-1
      DO 311 L1=1,NTOT
      IX=1
      CALL TAPE(KW,IX,JTB)
      IF(IX.EQ.13) GO TO 303
      CALL COMBIN(JTA,JTB,KINT,R,JMAX,REST)
  311 CONTINUE
      CALL COMBIN(JTB,JTB,KINT,R,JMAX,REST)
      IF(NTOT.EQ.1) GO TO 241
      NTOT=NTOT-1
      DO 312 L1=1,NTOT
      BACKSPACE KW
      BACKSPACE KW
      IX=1
      CALL TAPE(KW,IX,JTA)
      IF(IX.EQ.13) GO TO 303
      CALL COMBIN(JTA,JTB,KINT,R,JMAX,REST)
  312 CONTINUE
      GO TO 310
  241 WRITE(KINT) I,FINAL
      ENDFILE KINT
  242 REWIND KINT
      REWIND KW
```

```
      REWIND KR
  313 READ(KINT) L1,H2(L1)
      IF(H2(L1).NE.FINAL) GO TO 313
      REWIND KINT
      RETURN
  399 FORMAT(1H020X,18HINDICES DONT CHECK3(4X,2I4))
      END

**    ****    ****    ****    ****    ****    ****    ****    ****    ****    **
      SUBROUTINE COMBIN (JTA,JTB,NT,R,JMAX,OVP)
C     CONTROLS COMBINATION OF G(I,K) AND G(J,L)
      DIMENSION JTA(1460,4),JTB(1460,4)
      IND2(I,K)=MIN0(I,K)+(MAX0(I,K)*(MAX0(I,K)-1)/2)
      DO 1 I=1,4
      IF(JTA(11,I).EQ.0) GO TO 1
      K=4
      IF(JTB(11,1).EQ.JTA(11,1)) K=I
      DO 2 J=1,K
      IF(JTB(11,J).EQ.0) GO TO 2
      X=TWOEL(JTA(1,I),JTB(1,J),JTA(20,I),JTB(20,J),JTA(1,I),JTB(1,J),R,
     *JMAX,OVP)
      L1=IND2(JTA(11,I),JTB(11,J))
      WRITE(NT) L1,X
    2 CONTINUE
    1 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE TAPE(NO,KACT,JT)                                       TAP
C    PACKS,READS, AND WRITES INTEGRAL TABLES G(I,K)                     TAP
      DIMENSION JT(1460,4)                                              TAP
      GO TO (1,2),KACT                                                  TAP
    1 READ(NO) L,((JT(I,J),I=1,L),J=1,4)                                TAP
      RETURN                                                            TAP
    2 L=MAX0(JT(12,1),JT(12,2),JT(12,3),JT(12,4))                       TAP
      WRITE(NO)L,((JT(I,J),I=1,L),J=1,4)                                TAP
      RETURN                                                            TAP
      END                                                               TAP

**    ****    ****    ****    ****    ****    ****    ****    ****    ****
      SUBROUTINE ONEL(J1,J2,TAB,JTAB,JMAX)                              ONE
C    TAB LAYOUT - 1-7 NLP,8-J1,9-J2,10-EPOT,11-IND2,12-NWORDS,          ONE
C    13-16 FLP,17-S,18-EKIN,19-GINY,20-1460 GINT                        ONE
C   JTAB=TAB FOR PACKING AND UNPACKING  FIXED OR FLOAT WORDS.           ONE
      COMMON/SPACE/ZA,ZB,R,N,NHUG,NCON,MULT,KW,KR,KOR,NT,JNT,JCODE,     ONE
     1NPERMS,ND,NFCN,MMAT,N10,NMAT,NE,NPC,LSPARE,MSPARE,ITX,N1,NC1,NC2P,ONE
     2LSRCH,JKW3,LIAR,STEP1,STEP2,EO,NO,MO,IS,A1,A2,EFIN,SAVEA(9),MAD(2)ONE
     3 ,FPARO(2,16),FPAR(2,16),NFPAR(6,16),ITAG(16),ICTAG(6),LCON(6,8), ONE
     4DELT(25),RMAX,RMIN,RSTEP,STEP3                                    ONE
      COMMON/WORK/NLP(7),NOTA(5),FLP(4),S,H1,A(7),B(7),BINT(36,2),C(7,2)ONE
     1,DUMM(1326),          FL1,C2,C3,C5,C6,C7,KRONEK,EDELT,EZETA,EK1,  ONE
     2EK2,EK3,EK4,EK2PRI,EK3PRI,I,ZG1(1470) , RMDR(9588)                ONE
      DIMENSION TAB(1460), JTAB(1460)                                   ONE
      EQUIVALENCE (EPOT,NOTA(3 )),(EKIN,H1)                             ONE
      NOTA(1)=J1                                                        ONE
      NOTA(2)=J2                                                        ONE
      NOTA(5)=JTAB(12)                                                  ONE
      FLP(1)=FPAR(1,J1)+FPAR(1,J2)                                      ONE
      FLP(2)=FPAR(1,J1)-FPAR(1,J2)                                      ONE
      FLP(3)=FPAR(2,J1)+FPAR(2,J2)                                      ONE
      FLP(4)=FPAR(2,J1)-FPAR(2,J2)                                      ONE
      IF(ITX.EQ.1) GO TO 31                                             ONE
      IF(FLP(1).NE.TAB(13))GO TO 31                                     ONE
      IF(FLP(2).NE.TAB(14))GO TO 31                                     ONE
      IF(FLP(3).NE.TAB(15))GO TO 31                                     ONE
```

```
      IF(FLP(4).NE.TAB(16))GO TO 31
      RETURN
   31 NLP(1)=NFPAR(3,J1)-NFPAR(3,J2)
      NLP(2)=(IABS(NFPAR(3,J1))+IABS(NFPAR(3,J2))-IABS(NLP(1)))/2
      NLP(3)=NFPAR(2,J1)+NFPAR(2,J2)
C    NLP(4) OR L4 TO BE REDETERMINED BY BANDI IF ENTERED
      NLP(4)=JTAB(4)
      NLP(5)=NFPAR(1,J1)+NFPAR(1,J2)
      NLP(6)= NFPAR(2,J1)-NFPAR(2,J2)
      NLP(7)=NFPAR(1,J1)-NFPAR(1,J2)
      MMM        =NFPAR(2,J1)+NFPAR(3,J1)+NFPAR(4,J1)
      NNN        =NFPAR(2,J2)+NFPAR(3,J2)+NFPAR(4,J2)
      CALL BANDI(NNN,MMM)
      CALL GLIST(TAB(20), TAB(19),JMAX)
C     KRONECKER DELTA OVER NU(I),NU(J)
      IF(NLP(1).EQ.0) GO TO 65
      S=0.
      H1=0.
      EPOT=0.
      GO TO 53
C     KRONECKER DELTA OVER GERADE,UNGERADE
   65 IF(MOD(NHJG,2).EQ.0) GO TO 1331
      KRONEK= MMM+NNN+NLP(3)
      IF(MOD(KRONEK,2).EQ.0) GO TO 1331
      S=0.
      H1=0.
      EPOT=0.
      GO TO 53
C     APPENDIX I - EQN (40)
 1331  S=A(7)*B(5)-A(5)*B(7)
      C2=NLP(2)
      C3=NLP(3)
      C5=NLP(5)
      C6=NLP(6)
      C7=NLP(7)
```

```
C     APPENDIX I - EQN (41)
       EDELT=-A(6)*B(5)*(ZA+ZB)
C     APPENDIX I - EQN (42)
       EZETA= A(5)*B(6)*(ZA-ZB)
C     HERE TO STATEMENT 1332  - APPENDIX I - EQN. (43)
       EK1=B(5)*(FLP(2)*FLP(2)*A(7)-2.*(FLP(2)*C7+FLP(1))
      1*A(6)+2.*FLP(2)*C7*A(4)+(C5-C7*C7)*A(3))
       EK4=-4.0*C2*C2*(A(2)*B(1)-A(1)*B(2))
       EK2=-A(5)*(FLP(4)*FLP(4)*C(7,1)-2.*(FLP(4)*C6+FLP(3 ))*C(6,1)
      1+2.0*FLP(4)*C6*C(4,1)+(C3-C6*C6)*C(3,1))
       EK3=A(5)*C(5,1)*(C7*C7+C5-FLP(2)*FLP(2)-C6*C6-C3+FLP(4)*FLP(4))
       IF(MOD(NHJG,2).EQ.0) GO TO 1332
       FL1=1.
       IF(MOD(NNN,2).NE.0) FL1=-FL1
        EK2PRI=-A(5)*(FLP(3)*FLP(3)*C(7,2)-2.*(FLP(3)*C6+FLP(4))*C(6,2)
      1+2.*FLP(3)*C6*C(4,2)+(C3-C6*C6)*C(3,2))
       EK3PRI=A(5)*C(5,2)*(C7*C7+C5-FLP(2)*FLP(2)-C6*C6-C3+FLP(3)*FLP(3))
       EK2=EK2+FL1*EK2PRI
       EK3=EK3+FL1*EK3PRI
 1332  EKIN=EK1+EK2+EK3+EK4
       EPOT=EDELT+EZETA
   53  CONTINUE
       DO 55 I=1,18
   55  JTAB(I)=NLP(I)
       RETURN
       END
```

```
      FUNCTION TWOEL (TABA,TABB,G1,G2,NLP1,NLP2,R,NDIM,S)
C FUNCTION IS H2, OBTAINED BY MERGING THE 2 GINT LISTS,USING SIGMA AND
C  INDEX MAXIMA GIVEN IN NLP1 AND NLP2.
C  JMAX, NUMBER OF INTEGRATION POINTS, AND NMINUS, NUMBER TO BE
C  ACCUMULATED NEGATIVELY AT BEGINNING OF LIST, TO BE SUPPLIED
C  SEPARATELY AS CONSTANT INFORMATION.
C    APPENDIX I - EQN. (60), EXCEPT FOR KRONECKER DELTA OVER
C    SIGMA(1),-SIGMA(2), WHICH IS APPLIED IN FUNCTION TRX
      COMMON/DATBLS/D1(11,11),DD1(36,7),DD2(43,7),JMAX,WTINF,POINT(40),
     1WT(40),NMINUS,RULE(2)
      DIMENSIONTABA(1460),TABB(1460),NLP1(7),NLP2(7 )
      DIMENSION G1(NDIM,36),G2(NDIM,36) ,S(16)
 11   L= MIN0 (NLP1(4)-IABS (NLP1(1)),NLP2(4)-IABS (NLP2(1)))
      TWOEL=TABA(19)*TABB(19)
      L1 = NMINUS + 1
      DO 15 K=1,L
      IF(NMINUS.EQ.0) GO TO 16
   14 DO 13 K1=1,NMINUS
   13 TWOEL = TWOEL-G1(K1,K)*G2(K1,K)
   16 DO 15 K1 = L1,JMAX
   15 TWOEL = TWOEL+G1(K1,K)*G2(K1,K)
      TWOEL=2./R*TWOEL
      K=NLP1(8)
      L=NLP1(9)
      K1=NLP2(8)
      L1=NLP2(9)
      TWOEL=TWOEL/(S(K)*S(L)*S(K1)*S(L1))
      RETURN
      END
```

```
      SUBROUTINE BANDI (MMM,NNN)                                        BAI
C                                                                       BAI
C     GENERATES B AND BINT FOR PARAMETER ZETA                           BAI
C             A CONTAINS A INTEGRALS FOR ONE-ELECTRON CALCULATIONS      BAI
C                                                                       BAI
C    INPUT  L1 = NLP(1)=SIGMA=NU(I)+NJ(J)                               BAI
C           L2=TAU                                                      BAI
C           L3=M(I)+M(J)                                                BAI
C           L5=N(I)+N(J)                                                BAI
C     OUTPUT B   B(1) = B(MS) FOR TAU(1), B(2) = B(MS+2) FOR TAU(1)     BAI
C                B(3) TO B(7) = B(MS-2)TO B(MS+2) FOR NU1=NU2           BAI
C             BINT(K,L) BLOCK -  I  INTEGRAL. L=1 FOR I(MS),L=2, I(MS+2) BAI
C                K GIVES LOWER INDEX, VALUE OF 1 STARTS AT K=MUS.       BAI
C           L4=UPPER LIMIT OF MU SUMMATION IN NEUMANN EXPANSION         BAI
C     D(I,J)=FACT(FLOAT(I-1))*FLOAT(2*J-1)/DFACT(FLOAT(I-J))/DFACT(FLOATBAI
C    1(I+J-1))*(1.-FLOAT(I+J-((I+J)/2)*2))                              BAI
C     DD(I,J)=SQRT(FACT(FLOAT(I+J-2))*FLOAT(2*I-1)/FACT(FLOAT(I-J)))    BAI
C                                                                       BAI
      COMMON/SPACE/ IDUM(309)                                           BAI
      COMMON/WORK/L1,L2,L3,L4,L5,L6,L7,NOTA(5),DELT(2),ZETA(2),UL(2),   BAI
     *A(7),F(7),BINT(36,2),B(7,2),                                      BAI
     9S(38,11,2),R(60),                                                 BAI
     8      C,C1,J,K,L,M,K1,K2,K3,K4,K5,NIXIT,NUTS,IX,IY,IZ,NO,MMA,PAX, BAI
     7I,TEMP(426),ZG1(1470) , RMDR(9588)                                BAI
      COMMON/DAIBLS/D (11,11),DD (36,7),DD2(43,7),JMAX,WTINF,POINT(40), BAI
     1WT(40),NMINUS,RULE(2)                                             BAI
      DIMENSION X(60)                                                   BAI
      EQUIVALENCE(IDUM(5), NHUG)   ,(X,R),(LL,IX)  ,(DELTA,DELT(1))     BAI
      EQUIVALENCE(IDUM(22),IOUT)                                        BAI
      NIXIT = IABS(L1)                                                  BAI
      NO=1                                                              BAI
      DO 102 I=1,936                                                    BAI
  102 A(I)=0.                                                           BAI
      IF((L3.GT.8).OR.(L2.GT.3).OR.(NIXIT.GT.6)) GO TO 6                BAI
    1 IF( ABS(ZETA(NO)).GE.1.E-5) GO TO 1290                            BAI
```

```
C    MAKE I(0,ZETA,0) FOR VERY SMALL ZETA
      K1 = 2+NIXIT
      S(1,1,NO) = 2.
      DO 127 K=2,K1
      C=2*K-1
  127 S(K,1,NO) = -S(K-1,1,NO) / C
      S(K1,1,NO) = S(K1,1,NO)*ZETA(NO)
      K1  = K1+1
      DO1280 K=K1,38
 1280 S(K,1,NO) = 0.
      GO TO 1311
 1290 M=28.+ABS(ZETA(NO)/1.95)
      IF(M.GT.60) GO TO 6
C   MAKE I FOR M AND TAU ZERO
 1291 R(1) = 0.
      DO 1300 K=2,M
      C=2*(M-K)+3
 1300 R(K) = -ZETA(NO)/(C-ZETA(NO)*R(K-1))
      S(1,1,NO)=2.*EXP(ABS(ZETA(NO)))*ZETA(NO)**(-NIXIT)/(1.+ABS(ZETA(NO
     1))-ZETA(NO)*R(M))
      DO 1310 K=1,37
      L=M-K+1
 1310 S(K+1,1,NO) = S(K,1,NO)*R(L)
 1311 IF(MOD(NHUG,2).EQ.0) GO TO 100
C     MAKE I(M,ALFPRI,TAU) , APPENDIX I - EQN.(55)
      NO = NO+1
      IF(NO.EQ.2) GO TO 1
C   MAKE COEFFICIENTS FOR M AND TAU CALCULATION
  100 DO 1315 K=1,36
      C=K-NIXIT
      C1=2*K+1
 1315 R(K)=C/C1
C   ADVANCE TAU AND IF SIGMA ZERO, PREPARE B
      K4=37
      IF(L2.EQ.0) GO TO1400
```

```
 1320 K1=L2-1
 1325 IF(K1) 1400,1330,1340
 1330 IF(L1.NE.0) GO TO 1340
C  CALCULATE B FOR NU-1
 1332 K2=L3+1
      K3=L3-2*(L3/2)+1
      B(1,1)=0.
      B(1,2)=0.
      DO 1333 K=K3,K2,2
      DO 1333 NO=1,2
 1333 B(1,NO)=B(1,NO)+D(K2,K)*S(K,1,NO)
      K2=K2+2
      B(2,1)=0.
      B(2,2)=0.
      DO 1334 K=K3,K2,2
      DO 1334 NO = 1,2
 1334 B(2,NO)=B(2,NO)+D(K2,K)*S(K,1,NO)
 1340 K1=K1-1
C  ADVANCE TAU BY 1
 1350 DO 1360 J=1,2
      DO 1360 NO=1,2
      S(1,J+1,NO)=S(2,J,NO)
      K4=K4-1
      DO 1360 K=1,K4
 1360 S(K+1,J+1,NO)=(1.-R(K))*S(K+2,J,NO)+R(K)*S(K,J,NO)
      K5=K4+1
      DO 1370 K=1,K5
      DO 1370 NO=1,2
 1370 S(K,1,NO)=S(K,1,NO)-S(K,3,NO)
      GO TO 1325
 1400 IF(L1.NE.0) GO TO 1440
C  CALCULATE B FOR NU EQUALS NU
      K1=1
      IF(L3.GT.1) K1=L3-1
 1410 K2=L3+3
```

```
      DO 1420 J=K1,K2
      DO 1420 NO = 1,2
      K5=J-K2+7
      K3=J-2*((J-1)/2)
      B(K5,NO)=0.
      DO 1420 K=K3,J,2
 1420 B(K5,NO)=B(K5,NO)+D(J,K)*S(K,1,NO)
C  ADVANCE M TO FINAL VALUES
 1440 K2=L3+2
      DO 1450 J=1,K2
      DO 1450 NO = 1,2
      S(1,J+1,NO)=S(2,J,NO)
      K4=K4-1
      DO 1450 K=1,K4
 1450 S(K+1,J+1,NO)=(1.-R(K))*S(K+2,J,NO)+R(K)*S(K,J,NO)
      IF(MOD(NHUG,2).EQ.0) GO TO 1600
      PAX=1.
      IF((MMM-(MMM/2)*2).NE.0) PAX=-PAX
      DO 1501 IX=1,38
      DO 1501 IY=1,11
 1501 S(IX,IY,1)=   (S(IX,IY,1)+PAX*S(IX,IY,2))
      DO 1502 IX=1,7
 1502 F(IX)=B(IX,1)+PAX*B(IX,2)
C  MULTIPLY BY DD COEFFICIENTS
 1500 K5=K4+1
      K1=NIXIT + 1
      DO 1455 J=K1,K5
      S(J,K2-1,1) = DD(J,K1)*S(J,K2-1,1)
 1455 S(J,K2+1,1) = DD(J,K1)*S(J,K2+1,1)
C  TEST FOR CUT-OFF INDEX VALUE OR NON-CONVERGENCE
      C=0.
      DO 1460 K=K1,K5
 1460 C=AMAX1(C,ABS(S(K,K2-1,1)),ABS(S(K,K2+1,1)))
      C=1.E-5*C
      DO 1463 K=1,K5
```

```
      L4=K5+1-K                                                          BAI 1410
      IF(ABS(S(L4,K2-1,1)).GT.      C) GO TO 1470                        BAI 1420
      IF(ABS(S(L4,K2+1,1)).GT.      C) GO TO 1470                        BAI 1430
 1463 CONTINUE                                                           BAI 1440
 1470 IF(L4.EQ.K5) GO TO 1498                                            BAI 1450
C  FINAL STORAGE OF INTEGRALS                                            BAI 1460
 1471 IF(MOD(NHUG,2).EQ.0) GO TO 1504                                    BAI 1470
C    KRONECKER DELTA OF EQN. (55)                                        BAI 1480
      MMA=MMM+NNN+L3  - NIXIT                                            BAI 1490
      DO 1505 IX= K1,K5                                                  BAI 1500
      NUTS = MMA + IX -1                                                 BAI 1510
      NUTS=NUTS-(NUTS/2)*2                                               BAI 1520
      IF(NUTS.EQ.0) GO TO 1505                                           BAI 1530
      S(IX,K2+1,1) = 0.                                                  BAI 1540
      S(IX,K2-1,1) = 0.                                                  BAI 1550
 1505 CONTINUE                                                           BAI 1560
 1504 DO 1480 K=K1,L4                                                    BAI 1570
      J=K+1-K1                                                           BAI 1580
      BINT(J,1)=S(K,K2-1,1)                                              BAI 1590
 1480 BINT(J,2)=S(K,K2+1,1)                                              BAI 1600
      NOTA(5)=19+JMAX*(L4-NIXIT)                                         BAI 1610
C    MAKE A SUB N INTEGRALS - EQNS.(38,38PRIME,44)                       BAI 1620
      LL=L5+2*L2+2                                                       BAI 1630
      IF(NIXIT.NE.0) RETURN                                              BAI 1640
      X(1)=EXP (-DELTA)/DELTA                                            BAI 1650
      DO 1860 K=1,LL                                                     BAI 1660
      C=K                                                                BAI 1670
 1860 X(K+1)=X(1)+C*X(K)/DELTA                                           BAI 1680
      K5=L5+1                                                            BAI 1690
      IF(L2.EQ.0) GO TO 1890                                             BAI 1700
 1862 K3=L2-1                                                            BAI 1710
      K2=LL+1                                                            BAI 1720
 1863 IF(K3)1890,1864,1870                                               BAI 1730
 1864 A(1)=X(K5  )                                                       BAI 1740
      A(2)=X(K5+2)                                                       BAI 1750
```

```
 1870 K3=K3-1                                                          BAI 1760
      K2=K2-2                                                          BAI 1770
      DO 1880 K=1,K2                                                   BAI 1780
 1880 X(K)=X(K+2)-X(K)                                                 BAI 1790
      GO TO 1863                                                       BAI 1800
 1890 IF(L5-1) 1893,1892,1891                                          BAI 1810
 1891 A(3)=X(K5-2)                                                     BAI 1820
 1892 A(4)=X(K5-1)                                                     BAI 1830
 1893 A(5)=X(K5)                                                       BAI 1840
      A(6)=X(K5+1)                                                     BAI 1850
      A(7)=X(K5+2)                                                     BAI 1860
      RETURN                                                           BAI 1870
 1498 WRITE(IOUT,7)                                                    BAI 1880
      CALL EXIT                                                        BAI 1890
    6 WRITE(IOUT,9) L2,L3,NIXIT,M                                      BAI 1900
      CALL EXIT                                                        BAI 1910
    7 FORMAT(1H020X,17HBANDI-NO CONVERGE )                             BAI 1920
    9 FORMAT(1H020X,16HBANDI-PARAMS OUT 4I5)                           BAI 1930
C     B LOOP FOR HETERONUCLEAR CASE                                    BAI 1940
 1600 DO 1604 I=1,7                                                    BAI 1950
 1604 F(I) = B(I,1)                                                    BAI 1960
      GO TO 1500                                                       BAI 1970
      END                                                              BAI 1980
```

```
      SUBROUTINE GLIST(GINT,GT,NDIM)
C     INPUT-- SCREENING PARAMETER DELTA,MUST BE GREATER THAN +1.E-2.
C             BINT, LIST OF I INTEGRALS OUTPUT FROM BANDI PROGRAM
C             L1=SIGMA (MAY BE EITHER SIGN), L2=TAU, L5=N,
C             L4=MAXIMUM INDEX VALUE USED (STARTING FROM SIGMA=0). L4 IS
C                     PRODUCED AS OUTPUT IN BANDI PROGRAM.
C     OUTPUT-- GINT CONTAINS OUTPUT VALUES FOR TWO-ELECTRON INTEGRALS, IN
C                     A NUMBER DETERMINED BY L4 AND WPTBL(FROM GLIST PRO.).
C      USES CONSTANT DATA BLOCK DATBLS, ASSEMBLED SEPARATELY
C      /DATBLS/ CONTAINS NO. POINTS,BLOCK FOR 40 POINTS
C      BLOCK FOR CORRESPONDING 40 WEIGHTS, NO. OF INITIAL POINTS ENTERING
C     WITH MINUS SIGN IN SCALAR PRODUCT FORMATION.
C
C      ARRAY S(I,J)=K(MU,SIGMA) OF EQN. (56)
C      ARRAY GINT IS THE ARRAY OF G(I,K) INTEGRALS DEFINED BY
C      EQNS. (57-59)
C
C       D(I,J)=FLOAT(2*I-1)/FLOAT(I+J-1)
C       DD(I,J)=FLOAT(I+J-1)*FLOAT(I-J+1)/FLOAT(4*I*I-1)
        COMMON/SPACE/ IDUM(309)
        COMMON/WORK/L1,L2,L3,L4,L5,L6,L7,NOTA(5),DELTA,ZETA(5),A(7),B(7),
       *BINT(36,2),CX(7,2),
       2X(44),   FRAT(45,14),S(45,11),
       3      C,CC,R,TEE,L,J,LL,LM,LN,K,K1,K2,K3,K4,K5,K6,KK9,CL,CK,IP,
       4REST(153),ZG1(1470) ,RMDR(9588)
        COMMON/DATBLS/D1(11,11),DD1(36,7),DD (43,7),JMAX,WTINF,POINT(40),
       1WT(40),NMINUS,RULE(2)
        DIMENSION GINT(NDIM,36)
        EQUIVALENCE (IOUT,IDUM(22))
        DO 1984 J=1,1189
  1984  X(J)=0.
        LL=L5+2*L2+2
        LM=L4+LL
        LN=LM-1
        K1=IABS(L1)
```

```
      IF((L5.GT.8).OR.(LM.GE.45).OR.(DELTA.LT.0.01)) GO TO 11
      DO 1842 J=1,JMAX
      R=0.0
      TEE=DELTA*POINT(J)
      IF(TEE.LT.128.)R=WT(J)*EXP(-TEE)/DELTA
      TEE=TEE-DELTA
 1700 X(1)=POINT(J)
 1701 DO 1702 K=2,LM
 1702 X(K)=POINT(J)-DD(K-1,1)/X(K-1)
C  LARGE Y*DELTA.  KO AND K1
      S(1,1)=WT(J)*EXP (-DELTA)/DELTA - R
      S(2,1)=(S(1,1)*(DELTA+1.)/DELTA+R*(1.-POINT(J)))/POINT(J)
C  LARGE Y*DELTA.  REMAINING K
      DO 1710 K=2,LN
      C=K
 1710 S(K+1,1)=((S(K-1,1)+R)*C*(POINT(J)-X(K))/(C-1.)+C*S(K,1)/DELTA)/
     1 X(K)-R
      IF(K1.EQ.0) GO TO 1810
C NON-ZERO SIGMA. LARGE Y*DELTA.  MAKE F
 1720 K2=K1+1
      DO 1721 L=K2,LM
      FRAT(L,1)=1.0
      C=L
 1721 FRAT(L,2)=(X(L)*(2.0*C-1.0)/C-POINT(J))*DELTA/(C-1.0)
      KK9=K2-2
      IF(KK9) 1741,1741,1730
 1730 C=(POINT(J)**2-1.0)*DELTA
      DO 1740 L=K2,LM
      CL=L
      DO 1740 K=1,KK9
      CK=K
 1740 FRAT(L,K+2)=(-2.0*CK*POINT(J)*FRAT(L,K+1)+C*FRAT(L,K))*DELTA/((CL-
     1CK-1.0)*(CL+CK))
 1741 CONTINUE
C  LARGE Y*DELTA.  MAKE K SUB SIGMA
```

```
      DO 1760 K=K2,LM
      CC=FRAT(K,2)
      IF(K2-2) 1999,1750,1742
 1742 DO 1744 L=3,K2
 1744 CC=CC+FRAT(K,L)
 1750 C=K1
      IP = K1
 1760 S(K,1)=((SQRT(POINT(J)*POINT(J)-1.))**IP)*(S(K,1)*FRAT(K,1)-R*CC)/
     XFRAT(K,K2)
C  SEE IF NEW X COEFFICIENTS ARE NEEDED
      IF(K1.EQ.0) GO TO 1810
C NEW X COEFFICIENTS ARE NEEDED
 1800 C=K1
      X(1)=C+POINT(J)
      K2=K1+1
      DO 1803 K=2,LN
 1803 X(K)=POINT(J)-DD(K-1,K2)/X(K-1)
C  ADVANCE M AND TAU
 1810 K5=L2
      K2=K1+2
      K3=LM
      K4=K1+1
      IF(L2.EQ.0) GO TO 1830
 1811 K6=3
 1812 DO 1820 L=2,K6
      S(K1+1,L)=POINT(J)*S(K2,L-1)
      K3=K3-1
      DO 1820 K=K2,K3
 1820 S(K,L)=X(K)*S(K+1,L-1)+(POINT(J)-X(K))*S(K-1,L-1)
      K5=K5-1
      IF(K5) 1840,1822,1822
 1822 DO 1824 K=K4,K3
 1824 S(K,1)=S(K,3)-S(K,1)
      IF(K5) 1999,1830,1812
 1830 K6=L5+3
```

```
      GO TO 1812
C  COMBINE THESE RESULTS WITH I INTEGRALS
 1840 IF(K3.NE.L4) GO TO 1999
 1841 DO 1842 K=K4,K3
      L=K-K4+1
 1842 GINT(J,L)=S(K,K6)*BINT(L,1)-S(K,K6-2)*BINT(L,2)
C  POINT AT INFINITY
 1844 GT   = 0.
      IF(K1.EQ.0)GT=WTINF*(A(7)*BINT(1,1)-A(5)*BINT(1,2))
      RETURN
 1999 WRITE(IOUT,18)
      CALL EXIT
   11 WRITE(IOUT,19) DELTA,L5,LM
      CALL EXIT
   18 FORMAT(1H020X,17HGLIST-GENERAL ERR )
   19 FORMAT(1H020X,16HGLIST-PARAMS OUTF10.4,2I4)
      END

**    ****     ****     ****     ****     ****     ****     ****     ****     ****     **
      SUBROUTINE MATRIX (INPT,LCON,NUMBR,NEL)
C    CONTROLLING PROGRAM OF MATRIX    BRANCH
C   COMBINES UTAPE AND S1, H1, H2 TO MAKE TOTAL S, H
C    ZS1=S(P)  EQN (31)
C    ZH= H(P) EQN (32)
C    S1    EQN (35)
C    H1   EQN (34,37)
C    H2   EQN (36,60)
      COMMON/SPACE/ZA,ZB,R,N,NHUG,NCON,MULT,KW,KR,KOR,NT,JNT,JCODE,
     1NPERMS,ND,NFCN,MMAT,N10,NMAT,NE,NPC,LSPARE,MSPARE,ITX,N1,NC1,NC2P,
     2LSRCH,JKW3,LIAR,STEP1,STEP2,EO,NO,MO,IS,A1,A2,EFIN,SAVEA(9),MAD(2)
     3 ,FPARO(2,16),FPAR(2,16),NFPAR(6,16),ITAG( 6),ICTAG(64),
     4DELT(25),RMAX,RMIN,RSTEP,STEP3
      COMMON/WORK/H2(9317),UMAT(28,28),IPER(20),IDEN(3), I,J,K ,
     1L,L1,L2,L3,L4,K1,K2,K3,K4,K5,IP,II,JJ, IZ,ZS1,ZH ,IE1,IE2,ICON1,
     2 ICON2,KIK,KJL,DOM(19),S(903),H(903),SPRI(136),HPRI(136),S1(136),
     1H1(136)
      COMMON/CIJ/C(16,16),NOTRF,NU,MU,KRUD(9)
```

```
      EQUIVALENCE (OLP,H2),(HAM,H2(1765))
      EQUIVALENCE(IO,LSPARE)
      DIMENSION OLP(42,42),HAM(42,42), LCON(NUMBR,NEL)
C
      IND2(I,K)=MINO(I,K)+(MAXO(I,K)*(MAXO(I,K)-1)/2)
C
    1 FORMAT(8E15.7)
      NMAT=NCON*ND
      CALL TXFORM(SPRI,UMAT,IPER,DOM,NFPAR,ITX,NFCN,INPT,HPRI)
      CALL TRANS (S1,H1,SPRI,HPRI)
      IF(ITX.EQ.2) GO TO 1314
      L4=(MMAT*(MMAT+1))/2
      WRITE(IO,1) (S1(I),I=1,MMAT)
      WRITE(IO,1) (H1(I),I=1,MMAT)
      WRITE(IO,1) (H2(I),I=1,L4)
      IF(NOTRF.EQ.0) GO TO 1314
      WRITE(IO,1) (SPRI(I),I=1,MMAT)
      WRITE(IO,1) (HPRI(I),I=1,MMAT)
 1314 CONTINUE
      IZ=0
      L1=0
      DO 401 L=1,NMAT
      DO 401 K=1,L
      L1=L1+1
      H(L1)=0.
  401 S(L1)=0.
  410  CONTINUE
      READ(NT) IDEN
      IF(IDEN(3).NE. JCODE) GO TO 1999
      DO 411 IP=1,NPERMS
      READ (NT) (IPER(I),I=1,N),((UMAT(K,J),K=1,ND),J=1,ND)
      DO 412 ICON1=1,NCON
      II = (ICON1-1)*ND
      MU=ICON1
      IF((IABS(NHUG).EQ.2).AND.(ICON1.GT.(NCON/2))) MU=NCON/2
```

```
      DO 412 ICON2=1,MU
      JJ =(ICON2-1)*ND
  406 IZ = 0
      ZS1 = 1.
      DO 413 IE1 = 1,N
      I = LCON(ICON1,IE1)
      L1 = IPER(IE1)
      K = LCON(ICON2,L1)
      L2=IND2(I,K)
      IF(S1(L2).EQ.0.)  GO TO 414
      ZS1 = ZS1*S1(L2)
      GO TO 413
  414 IZ = IZ+1
      IF (IZ-2) 415,416,412
  415 K1=I
      K2=K
      K5=IE1
      KIK=L2
      GO TO 413
  416 K3=I
      K4=K
      KJL=L2
  413 CONTINUE
      IF(IZ-1) 420,421,422
C     NO OVERLAP WAS ZERO
  420 ZH = 0.
      DO 423 IE1=1,N
      I = LCON(ICON1,IE1)
      L1 =IPER(IE1)
      K=LCON(ICON2,L1)
      L2 = IND2(I,K)
      ZH=ZH+H1(L2) /S1(L2)
      DO 419 IE2=1,IE1
      IF(IE1.EQ.IE2)  GO TO 423
      J=LCON(ICON1,IE2)
```

```
      L3 = IPER(IE2)
      L =LCON(ICON2,L3)
  419 ZH=ZH+TRX(I,J,K,L,H2,S1)
  423 CONTINUE
      GO TO 426
C     ONE OVERLAP INTEGRAL = 0.  ELECTRON NO. STORED IN L3
  421 ZH=H1(KIK)
      DO 425 IE2=1,N
      IF(IE2.EQ.K5) GO TO 425
      J=LCON(ICON1,IE2)
      L1=IPER(IE2)
      L=LCON(ICON2,L1)
      ZH=ZH+TRX(K1,J,K2,L,H2,S1)
  425 CONTINUE
      GO TO 426
C     TWO FACTORS WITH ZERO OVERLAP
  422 ZH=TRX(K1,K3,K2,K4,H2,S1)
      IF(ZH.EQ.0.) GO TO 412
  426 ZH=ZH*ZS1
C    STORE ZS1,ZH*UMAT(I,J) IN D*D BLOCKS, INDEXED AS A ROW VECTOR
      DO 424 I=1,ND
      L1 = II+I
      L1=(L1*(L1-1))/2
      KJL=ND
      IF(II.EQ.JJ) KJL=I
      DO 424 J=1,KJL
      L2=JJ+J+L1
      IF (IZ. GT.0) GO TO 424
      S(   L2)= S(   L2) + UMAT(I,J)*ZS1
  424 H(   L2)= H(   L2) + UMAT(I,J)*ZH
  412 CONTINUE
  411 CONTINUE
      L1=0
      DO 500 I=1,NMAT
      DO 500 J=1,I
```

```
      L1=L1+1
      HAM(I,J)=H(L1)
      OLP(I,J)=S(L1)
      OLP(J,I)=S(L1)
  500 HAM(J,I)=H(L1)
C     INVERT TOTAL MOLECULAR FUNCTION AND PICK G OR U - EQN (16)
      IF(IABS(NHUG).NE.2) RETURN
      KIK=NCON/2
      KJL=NMAT/2
      DO 512 ICON1=1,KIK
      II=(ICON1-1)*ND
      JJ=II+KJL
      IZ=0
      DO 513 I=1,N
      J=LCON(ICON1,I)
  513 IZ=IZ+NFPAR(2,J)+NFPAR(3,J)
      IP=ISIGN(1,NHUG)
      IF(MOD(IZ,2).NE.0) IP=-IP
      ZH=IP
      DO 514 I=1,ND
      L1=II+I
      L2=JJ+I
      DO 514 J=1,KJL
      OLP(L1,J)=OLP(L1,J)+ZH*OLP(L2,J)
  514 HAM(L1,J)=HAM(L1,J)+ZH*HAM(L2,J)
  512 CONTINUE
      NMAT=NMAT/2
C     HAM,OLP ARE CARRIED OVER INTACT TO SEARCH
      RETURN
C     FORTRAN TAPE ROCKING MACRO TO CORRECT TAPE POSITION ERRORS
C     CONSISTENTLY MADE BY HONEYWELL AUTOMATH 1800 MONITOR
 1999 IF(IZ.EQ.1313) CALL EXIT
      WRITE(IO,105) JCODE,IDEN(3)
      IZ=1313
      REWIND NT
```

```
      GO TO 410
  105 FORMAT(1H020X,15HWRONG PERM TAPE2I6)
      END

**    ****     ****     ****     ****     ****     ****     ****     ****     ****     **
      SUBROUTINE TXFORM(S1,S,NORD,IORD,NFPAR,ITX,N,IN,H1)
C     PREPARE TRANSFORMATIOM MATRIX
C    THE TAG NOTRF DETERMINES THE TYPE TRANS.
C    NOTRF.LT.0  -  CONSTANT TRANS BY INPUT CARDS
C    NOTRF=0    - NO TRANSFORMATION
C     NOTRF .GT. ZERO  - TRANSFORMATION IS TO BE CALCULATED
      COMMON/CIJ/C(16,16),NOTRF,NU,MU,I,J,K,L,HH,JUNK(4)
      DIMENSION S1(136),S(16,16),NORD(16),IORD(16),NFPAR(6,16)
      DIMENSION H1(136)
      IND2(I,K)=MINO(I,K)+(MAXO(I,K)*(MAXO(I,K)-1)/2)
      IF(NOTRF.LE.0) RETURN
   50 IF(NOTRF.EQ.1) GO TO 54
      L=0
      DO 55 I=1,N
      DO 55 J=1,I
      L=L+1
   55 S(J,I)=S1(L)
      GO TO 63
   54 L=0
      DO 51 I=1,N
      DO 51 J=1,I
      L=L+1
      S(I,J)=0.
      S(J,I)=0.
      IF(I.EQ.J) S(I,I)=S1(L)
   51 CONTINUE
      K=NU+1
      DO 52 I=K,N
      DO 52 J=1,NU
      IF(NFPAR(5,I).EQ.0) GO TO 52
      L=IND2(I,J)
      S(J,I)=S1(L)
```

```
52 CONTINUE
63 NORD(1)=1313
   CALL D23CHO(N,S,C,C,C,IORD,NORD,16)
   DO 64 I=1,N
   DO 64 J=1,N
64 C(I,J)=S(J,I)
   RETURN
   END

**    ****    ****    ****    ****    ****    ****    ****    ****    ****    **
      SUBROUTINE TRANS (SPRI,HPRI,S1,H1)
C   APPLIES A TRANSFORMATION C(I,J) IN /CIJ/ TO H1,S1, STORING
C   THE RESULT IN THE LAST 272 WORDS OF /WORK/
C   TRANSFORMATION IS SUPPLIED ELSEWHERE BY INPUT CONSTANTS OR CALC.
      COMMON/SPACE/ZA,ZB,R,N,NHUG,NCON,MULT,Kw,KR,KOR,NT,JNT,JCODE,
     1NPERMS,ND,NFCN,MMAT,N10,NMAT,NE,NPC,LSPARE,MSPARE,ITX,N1,NC1,NC2P,
     2LSRCH,JKW3,LIAR,STEP1,STEP2,EO,NO,MO,IS,A1,A2,EFIN,SAVEA(9),MAD(2)
     3 ,FPARO(2,16),FPAR(2,16),NFPAR(6,16),ITAG(16),ICTAG(6),LCON(6,8),
     4DELT(25),RMAX,RMIN,RSTEP,STEP3
      COMMON/CIJ/C(16,16),NOTRF,NU,MU,I,J,K,L,L1,HH,SS,CO,SAM
      DIMENSION S1(136),H1(136),SPRI(136),HPRI(136)
      IND2(I,K)=MINO(I,K)+(MAXO(I,K)*(MAXO(I,K)-1)/2)
      IF(NOTRF.NE.0) GO TO 10
      DO 11 I=1,MMAT
      HPRI(I)=H1(I)
   11 SPRI(I)=S1(I)
      RETURN
   10 L1=0
      SAM=1.E+10
      DO 1 I=1,NFCN
      DO 1 K=1,I
      L1=L1+1
      HH=0.
      SS=0.
      DO 2 J=1,NFCN
      IF(C(I,J).EQ.0.) GO TO 2
      DO 3 L=1,NFCN
```

```
      IF(C(K,L).EQ.0.) GO TO 3
      INDX=IND2(J,L)
      CO = C(I,J)*C(K,L)
      SS=SS+CO*S1(INDX)
      HH=HH+CO*H1(INDX)
    3 CONTINUE
    2 CONTINUE
      IF((K.EQ.I).AND.(SS.LT.SAM)) SAM=SS
      SPRI(L1)=SS
      HPRI(L1)=HH
    1 CONTINUE
      SAM=1.E-7*SAM
      DO 4 I=1,MMAT
      IF(SPRI(I).LE.SAM) SPRI(I)=0.
    4 CONTINUE
      RETURN
      END

**    ****    ****    ****    ****    ****    ****    ****    ****    ****     **
      FUNCTION TRX(I,J,K,L,H2,S1)
C    CALCULATES THE TRANSFORMED TWO-ELECTRON INTEGRALS UNDER THE
C    TRANSFORM C(I,J) STORED IN /CIJ/
C    THE TRANSFORM IS DEFINED AS FOLLOWS  X(K)=(SUM(L)) OF(C(K,L)*XPRI(L)
      COMMON/SPACE/ZA,ZB,R,N,NHUG,NCON,MULT,KW,KR,KOR,NT,JNT,JCODE,
     1NPERMS,ND,NFCN,MMAT,N10,NMAT,NE,NPC,LSPARE,MSPARE,ITX,N1,NC1,NC2P,
     2LSRCH,JKW3,LIAR,STEP1,STEP2,EO,NO,MO,IS,A1,A2,EFIN,SAVEA(9),MAD(2)
     3 ,FPARO(2,16),FPAR(2,16),NFPAR(6,16),ITAG(16),ICTAG(6),LCON(6,8),
     4DELT(25),RMAX,RMIN,RSTEP,STEP3
      COMMON/CIJ/C(16,16),NOTRF,NU,MU,I1,J1,K1,L1,IDX1,IDX2,IDX3,M1,M2
      DIMENSION H2(9317),S1(136)
      IND2(I,K)=MIN0(I,K)+(MAX0(I,K)*(MAX0(I,K)-1)/2)
      TRX=0.
      M1=IND2(I,K)
      M2=IND2(J,L)
      IF(NOTRF.NE.0) GO TO 10
      IF((NFPAR(3,I)-NFPAR(3,K)+NFPAR(3,J)-NFPAR(3,L)).NE.0) RETURN
      IDX1=IND2(M1,M2)
```

```
      TRX=H2(IDX1)
      GO TO 11
   10 DO 1 I1=1,NFCN
      IF(C(I,I1).EQ.0.) GO TO 1
      DO 2 J1=1,NFCN
      IF(C(J,J1).EQ.0.) GO TO 2
      DO 3 K1=1,NFCN
      IF(C(K,K1).EQ.0.) GO TO 3
      DO 4 L1=1,NFCN
      IF(C(L,L1).EQ.0.) GO TO 4
      IF((NFPAR(3,I1)-NFPAR(3,K1)+NFPAR(3,J1)-NFPAR(3,L1)).NE.0) GO TO 5
      IDX1=IND2(I1,K1)
      IDX2= IND2(J1,L1)
      IDX3= IND2(IDX1,IDX2)
      TRX=TRX+C(I,I1)*C(J,J1)*C(K,K1)*C(L,L1)*H2(IDX3)
    5 CONTINUE
    4 CONTINUE
    3 CONTINUE
    2 CONTINUE
    1 CONTINUE
   11 IF(NOTRF.GT.0) RETURN
      IF(S1(M1).NE.0.) TRX=TRX/S1(M1)
      IF(S1(M2).NE.0.) TRX=TRX/S1(M2)
      RETURN
      END
```

```
      SUBROUTINE SEARCH
C     CONTROLLING PROGRAM OF SEARCH    BRANCH
C
C     ENERGY CALCULATION AND PARAMETER SEARCH LINK
C
      COMMON/SPACE/ZA,ZB,R,N,NHUG,NCON,MULT,KW,KR,KOR,NT,JNT,JCODE,
     1NPERMS,ND,NFCN,MMAT,N10,NMAT,NE,NPC,LSPARE,MSPARE,ITX,N1,NC1,NC2P,
     2LSRCH,JKW3,LIAR,STEP1,STEP2,E0,NO,MO,IS,A1,A2,EFIN,SAVEA(9),MAD(2)
     3 ,FPAR0(2,16),FPAR(2,16),NFPAR(6,16),ITAG(16),ICTAG(6),LCON(6,8),
     4FELT(25),RMAX,RMIN,RSTEP,STEP3
      COMMON/WORK/OVRLAP(42,42),HAMILT(42,42),COET(42,42),COETO(42,42),
     *OVP(42,42),HAM(42,42),E(42),E1(42),E2(42),E3(42),KO,I,J,TEMP,NE1,
     XFINK(1760),SIG
      COMMON/DAIBLS/D1(11,11),DD1(36,7),DD2(43,7),JMAX,WTINF,POINT(40),
     1WT(40),NMINUS,RULE(2)
      COMMON/CIJ/C(16,16),NOTRF,NU,MU,KRUD(9)
      DIMENSION D(6),Z(6),ENERG(6),X(2),Y(2),A(6)
      EQUIVALENCE(D,FELT(1)),(X,E1),(Y,E2),(A,E3),(Z,ENERG),(Z,FELT(7))
      EQUIVALENCE(DELT,FELT(25))
      EQUIVALENCE (MSPARE,ID)
      EQUIVALENCE (ID,LSPARE)
      EQUIVALENCE (ITAG(5),PA)
      DIMENSION  AG(2)
 1984 DATA ( AG(I),I=1,2)/6HOVRLAP,6HHAMILT/
  109 FORMAT(13X,  5HFPAR(I2,1H,I2,2H)=F10.5,4X,4HNC1=I5)
  104 FORMAT(1H0,10HPARAMETERS /)
  105 FORMAT(5X,I3,2F12.6,3X,6I3)
  106 FORMAT(1H0,(13X,7E15.7))
  107 FORMAT(1H0,10X,3HE =E16.8,7H   FCN(I2,1H,I2,7H)  KOR=I3,
     *8H   STEPS  2F14.6)
  305 FORMAT(1H0,20X,A6,1X,6HMATRIX)
      DO 101 I=1,NMAT
      DO 101 J=1,I
      OVP(I,J)=OVRLAP(I,J)
      OVP(J,I)=OVRLAP(I,J)
```

```
      OVRLAP(J,I)=OVRLAP(I,J)
      HAM(I,J)= HAMILT(I,J)
      HAM(J,I)= HAMILT(I,J)
  101 HAMILT(J,I)=HAMILT(I,J)
      WRITE(IO,104)
      DO 110 J=1,NFCN
  110 WRITE(IO,105)J,FPAR(1,J),FPAR(2,J),(NFPAR(I,J),I=1,6)
      E2(1)=0.
      CALL D23CHO(NMAT,OVP    ,HAM    ,COET,COETO,E,E2,ID)
      NE1=NE+1
      IF(EFIN.EQ.0.) GO TO 1000
      IF(E(NE1).GT.EFIN) GO TO 1000
      WRITE(IO,1003)
 1003 FORMAT(1H020X,14HENERGY.LT.MIN.)
      GO TO 531
 1000 CONTINUE
      WRITE(IO,106)(E(I),I=1,NMAT)
      WRITE(IO,107)E(NE1),NO,MO,KOR,STEP1,STEP2
 1005 GO TO (200,400,262,200), ITX
  200 CONTINUE
      IF(KR.NE.0) GO TO 2
      KR=KW
      KW=KOR
      GO TO 3
    2 KO=KR
      KR=KW
      KW=KO
    3 N10=N
  412 EO=E(NE1)
      IF(NPC.EQ.0) GO TO 53
      KO= MO+NFCN/2
      IF(NOTRF.EQ.1) KO=MO+(NFCN-NU)/2
      WRITE(IO,305)  AG(1)
      CALL PMA(OVRLAP,NMAT,E3,0,E,ID,IO)
      WRITE(IO,305)  AG(2)
```

```
      CALL PMA(HAMILT,NMAT,E3,0,E,ID,IO)
      ITX=2
       KOR=0
      GO TO 401
  400 KO= MO+NFCN/2
      IF(NOTRF.EQ.1) KO=MO+(NFCN-NU)/2
      IF(E(NE1).GE.E0) GO TO 401
      MU=KR
      KR=KW
      KW=MU
      FPARO(NO,MO)=FPAR(NO,MO)
      IF(ITAG(4).NE.0) FPARO(NO,KO   )=FPAR(NO,KO   )
      E0=E(NE1)
 401  KOR=KOR+1
      CALL SSWTCH(4,IREX)
      IF(IREX.EQ.2) GO TO 403
      RMAX=RMIN
      LIAR=1
      GO TO 62
  403 IF(LSRCH.EQ.0) GO TO 402
C    LINEAR STEP SEARCH ONLY
      IF(KOR.EQ.LSRCH) GO TO 804
  805 FPAR(NO,MO)=FPAR(NO,MO)+STEP1
      GO TO 11
  804 FPAR(NO,MO)=FPARO(NO,MO)
      GO TO 40
  402 CONTINUE
      CALL SSWTCH(5,IREX)
      IF(IREX.EQ.1) GO TO 998
      ENERG(KOR) = E(NE1)
      IF((NO.EQ.2).AND.(IS.LE.1)) GO TO 500
 1500 D(KOR)=FPAR(NO,MO)
      GO TO (10,20,31,540), KOR
C     DELTA SEARCH
   10 PA=1.
```

```
 21 FPAR(NO,MO)=D(KOR) + PA*STEP1                                        SCH 1060
 11 SIG=1.                                                               SCH 1070
    IF((ZA.EQ.ZB).AND.(MOD(NHUG,2).EQ.0)) SIG=-1.                        SCH 1080
 12 IF(FPAR(1 ,MO).LT.0.01) FPAR(1 ,MO)=.01                              SCH 1090
    IF(ABS(FPAR(2,MO)).GT.1.1*FPAR(1,MO)) FPAR(2,MO)=SIGN(1.1*FPAR(1,MSCH 1100
   *O),FPAR(2,MO))                                                       SCH 1110
    IF(ITAG(4).EQ.0) GO TO 241                                           SCH 1120
    FPAR(1,KO)=FPAR(1,MO)                                                SCH 1130
    FPAR(2,KO)=SIG*FPAR(2,MO)                                            SCH 1140
241 RETURN                                                               SCH 1150
 20 IF(Z(2).LT.Z(1)) GO TO 21                                            SCH 1160
    PA=-1.                                                               SCH 1170
    FPAR(NO,MO)=D(1)+ PA*STEP1                                           SCH 1180
    GO TO 11                                                             SCH 1190
 31 IF(Z(3).GT.EO) GO TO 30                                              SCH 1200
    IF(ABS(FPAR(NO,MO)).LT.0.011) GO TO 30                               SCH 1210
    IF(ABS(FPAR(2,MO)).GT.(1.09*FPAR(1,MO))) GO TO 30                    SCH 1220
 33 Z(1)=Z(2)                                                            SCH 1230
    Z(2)=Z(3)                                                            SCH 1240
    D(1)=D(2)                                                            SCH 1250
    D(2)=D(3)                                                            SCH 1260
    KOR=2                                                                SCH 1270
    PA=1.5*PA                                                            SCH 1280
    GO TO 21                                                             SCH 1290
 30 A(5)=0.                                                              SCH 1300
    DO131 I=1,3                                                          SCH 1310
    X(I)=D(I)*D(I)                                                       SCH 1320
    Y(I)=D(I)                                                            SCH 1330
131 CONTINUE                                                             SCH 1340
    A(1)=Z(1)*(Y(2)-Y(3))+Y(1)*(Z(3)-Z(2))+Z(2)*Y(3)-Y(2)*Z(3)           SCH 1350
    A(2)=X(1)*(Z(2)-Z(3))+Z(1)*(X(3)-X(2))+X(2)*Z(3)-Z(2)*X(3)           SCH 1360
    DELT=-.5*A(2)/A(1)                                                   SCH 1370
    WRITE(IO,109) NO,MO,DELT,NC1                                         SCH 1380
    IF(A(1)/((D(1)-D(2))*(D(1)-D(3))*(D(2)-D(3))))   35,999,32           SCH 1390
 32 FPAR (NO,MO)=DELT                                                    SCH 1400
```

```
      DO 34 I=1,3
      IF(ABS(DELT-D(I)).LT.1.E-5) GO TO 40
   34 CONTINUE
      GO TO 11
  999 NFPAR(6,MO)=1
      IF(NO.EQ.2) NFPAR(6,MO)=2
   40 KOR=1
      PA=1.
      Z(1)=EO
      FPAR(NO,MO)=FPARO(NO,MO)
      IF(ITAG(4).NE.0) FPAR(NO,KO   )=FPARO(NO,KO   )
   41 IF(NO.EQ.2) GO TO 60
      IF(NFPAR(6,MO).GE.2) GO TO 60
      NO=NO+1
      D(1)=FPAR(NO,MO)
      IF(IS.GT.1) GO TO 10
C     INITIAL ALPHA SEARCH
  500 GO TO (510,520, 30,540), KOR
  510 D(3)=D(1)/2.
      D(2)=D(1)+D(3)
      FPAR(NO,MO)=D(2)
      GO TO 11
  520 FPAR(NO,MO)=D(3)
      GO TO 11
  540 NC2P=0
      DO 541 I=1,4
      IF(ABS((Z(I)-Z(4))/Z(4)).LT.1.E-5) NC2P=NC2P+1
  541 CONTINUE
C     SET TAG IF ENERGY IS INDEPENDENT OF PARAMETER
      IF(NC2P.EQ.4) NFPAR(6,MO)= NO + NFPAR(6,MO)
      GO TO 40
   60 IF(MO.EQ.NPC) GO TO 61
      MO=MO+1
      KO=KO+1
      NO =1
```

```
      IF((NFPAR(6,MO).EQ.1).OR.( NFPAR(6,MO).GE.3))      GO TO 41
      D(1)=FPAR(NO,MO)
      GO TO 10
 61   IF(STEP1.LE.STEP2) GO TO 62
      STEP1=.3*STEP1
      IF(STEP1.LT.STEP2) STEP1=STEP2
      LSRCH=0
   65 IS=IS+1
   64 MO=1
      NO = 1
      IF(NOTRF.EQ.0) NU=0
      MO=MO+NU
      KO=(NFCN-NU) /2 +1
      D(1)=FPAR(NO,MO)
      GO TO 10
 62   ITX=3
      DO 63 I=1,2
      DO 63 J=1,16
  63  FPAR(I,J)=FPARO(I,J)
      RETURN
 262  CONTINUE
   53 CONTINUE
  531 ITX=0
      RETURN
   35 WRITE(IO,108)
  108 FORMAT(1HO20X,17HGR.SRCH SEEKS MAX )
      GO TO 40
  997 FORMAT(1HO10X,15HEND SRCH OF FCN  2I4//)
  998 WRITE(IO,997) NO,MO
C    THIS CANNOT BE DONE ON IBM 7094
      PAUSE 998
      NFPAR(6,MO)=NO  + NFPAR(6,MO)
      GO TO 40
      END
```

```
      SUBROUTINE D23CHO (N,S,H,P,C,E,NN,ID)
C     SOLVES GENERAL SECULAR EQUATION (H-ES)=0 WHERE S NEED NOT BE DIAGON
C     AL, BY CHOLESKY-BANACHIEWICZ ALGORITHM
C     IF NN(1) IS SET TO 1313 PRIOR TO ENTRY, PROGRAM DETERMINES LINEAR
C     TRANSFORMATION TO ORTHONORMALIZE BASIS SET  WHOSE GRAM DETERMINANT
C     IS STORED IN ARRAY NAMED S
      DIMENSION S(ID,ID),H(ID,ID),P(ID,ID),C(ID,ID),E(ID),NN(ID)
      EQUIVALENCE (NT,L),(NTA,K)
  120 FORMAT(1H020X,18HOVRLAP NOT POS DEFE15.7,2I4)
      IF(N.GT.1) GO TO 100
      E(1)=H(1,1)/S(1,1)
      P(1,1)=1.
      RETURN
C     CALCULATE UPPER TRIANGULAR MATRIX
  100 DO 10 I=1,N
      L = I-1
      DO 10 J=I,N
      HH = S(I,J)
      IF(L.EQ.0) GO TO 5
    3 DO 4 K=1,L
    4 HH = HH - S(K,J)*S(K,I)
    5 IF(I.EQ.J) GO TO 7
    6 S(I,J) = HH/S(I,I)
      GO TO 10
    7 IF(HH.GT.1.E-5) GO TO 75
C IBM COMMON/SPACE/KLUTZ(309)
C IBM EQUIVALENCE (IOUT,KLUTZ(22))
C IBM WRITE(IOUT,120) HH,I,J  INSTEAD OF PRINT STATEMENT
      PRINT 120, HH,I,J
      IF(HH.GT.0.) GO TO 75
      IF(NN(1).EQ.1313) CALL EXIT
      IF(ABS(HH).LT.1.E-7) GO TO 74
      CALL EXIT
   74 DO 30 K=1,N
      S(I,K) = 0.
```

```
      S(K,I) = 0.
      H(K,I) = 0.
   30 H(I,K) = 0.
      S(I,I) = 1.0E-10
      H(I,I) = 1.0E+5
      GO TO 10
   75 S(I,J) = SQRT(HH)
   10 CONTINUE
C     INVERSE MATRIX   IN UPPER TRIANGLE
      DO 18 J=1,N
      L = J-1
      DO 18 I=1,N
      IF(I-J) 12,11,20
   20 S(I,J) = 0.
      GO TO 18
   11 S(J,J) = 1.0 / S(J,J)
      GO TO 18
   12 HH = 0.
   13 DO 14 K=1,L
   14 HH = HH-S(K,J)*S(I,K)
   15 S(I,J) = HH/S(J,J)
   18 CONTINUE
      IF(NN(1).EQ.1313) RETURN
C     TRANSFORM H-MATRIX
      DO 29 I=1,N
      DO 29 J=I,N
      HH = 0.
      DO 28 K=1,I
      DO 27 L=1,J
      HH = HH+S(L,J)*S(K,I)*H(K,L)
   27 CONTINUE
   28 CONTINUE
      P(J,I) = HH
   29 P(I,J) = HH
      CALL EIG(N,P,C,ID)
```

```
      N1=N
      DO 2 I=1,N1
      E(I)=P(I,I)
    2 NN(I)=I
      IF (N1.EQ.1)  GOTO40
      NT=N1
 1    NT=NT-1
      NTA=0
C    ORDER EIGENVALUES AND EIGENVECTORS
      DO 33 J=1,NT
      IF((E(J+1)-E(J)).GE.0.) GO TO 33
      HH=E(J+1)
      E(J+1)=E(J)
      E(J) = HH
      I=NN(J+1)
      NN(J+1)=NN(J)
      NN(J)=I
      NTA=1
 33   CONTINUE
      IF(NTA.EQ.1) GO TO 1
C     TRANSFORM C TO P
   40 DO 21 J=1,N
      NT=NN(J)
      DO 21 I=1,N
      HH=0.
      DO 22 K=I,N
   22 HH=HH+S(I,K)*C(K,NT)
   21 P(I,J) = HH
      RETURN
      END
```

```
      SUBROUTINE    EIG  (N,H,C,ID)
C   FINDS EIGENVALUES AND COLUMN EIGENVECTORS BY JACOBI METHOD
C   INPUT MATRIX IS H, EIGEN VALUES RETURNED IN H(I,I)
C   VECTOR MATRIX IS C, SET TO IDENTITY MATRIX IN THIS ROUTINE
      DIMENSION H(ID,ID),C(ID,ID)
      IF(N.EQ.1) RETURN
C     ENTER UNITY-MATRIX
      DO 99 I1=1,N
      DO 98 J1=1,N
   98 C(I1,J1)=0.
   99 C(I1,I1)=1.
      SIG=N *N
      TR=0.
      DO 1 I1=2,N
      M=I1-1
      DO 1 J1=1,M
      H(J1,I1)=H(I1,J1)
 1    TR=TR+ABS(H(I1,J1))
      IF(TR.EQ.0.) RETURN
      SUM=TR
      THRESH=1.E-15*TR
  105 TR=SUM/SIG
 107  LTAG=0
      SUM=0.
      M = N-1
      KKK=0
      DO 137 K=1,M
      KKK=KKK+1
      L=K+1
      DO 137 J1=KKK,K
      DO 137 I1=L,N
      SUM=SUM+ABS(H(I1,J1))
 115  IF(ABS(H(I1,J1)).LE.TR) GO TO 137
      LTAG=1
      P=1.
```

```
      X=-H(I1,J1)
      CC=.5*(H(I1,I1)-H(J1,J1))
      IF(CC.LT.0.) P=-P
      P=P*X/SQRT(X*X+CC*CC)
      CC=SQRT(1.-P*P)
      S=P/SQRT(2.*(1.+CC))
      SS=S*S
      CC=1.-SS
      X=SQRT(CC)
      S2=2.*X*S
C     TRANSFORM 2X2 BLOCK
      P=H(I1,I1)+H(J1,J1)
      CC      =H(I1,I1)*CC-H(I1,J1)*S2+H(J1,J1)*SS
      SS=P-CC
      DO 242 JP=1,N
      P=H(I1,JP)
      H(I1,JP)=P*X-H(J1,JP)*S
      H(J1,JP)=P*S+H(J1,JP)*X
      H(JP,I1)=H(I1,JP)
      H(JP,J1)=H(J1,JP)
      P=C(JP,I1)
      C(JP,I1)=P*X-C(JP,J1)*S
      C(JP,J1)=P*S+C(JP,J1)*X
  242 CONTINUE
      H(I1,I1)=CC
      H(J1,J1)=SS
      H(J1,I1)=0.
      H(I1,J1)=0.
 137  CONTINUE
      IF(LTAG.EQ.1) GO TO 107
      IF(SUM.GT.THRESH)  GO TO 105
      RETURN
      END
```

```
      SUBROUTINE    PMA  (A,N,NN,NBOOL,E,ID,KO)
C    PRINTS MATRICES AND ARRAYS
C     NBOOL = 0 SYMMETRIC, PRINT LOWER TRIANGLE
C     NBOOL = 1 UNSYMMETRIC MATRIX, E(I) IS NOT PRINTED
C     NBOOL = 2  UNSYMMETRIC MATRIX, PRINT OF VECTOR E
C     KO= IDENT. OF COMMON OUTPUT DEVICE(TAPE,DISC)
      DIMENSION A(ID,ID),NN(ID),E(ID)
  101 FORMAT(1H0,10X,7(I10,5X) )
  102 FORMAT(I7,3X,7E15.7)
  103 FORMAT (/)
  104 FORMAT (10X,7E15.7)
      DO 13 I=1,N
   13 NN(I) = I
      LPM = 7
      DO 8 JA = 1,N,LPM
      JE = JA+LPM-1
      IF (N.LT.JE)  JE = N
    3 WRITE(KO,101)(NN(J),J=JA,JE)
      WRITE(KO,103)
      IF (NBOOL .LT.2)  GO TO 15
      WRITE(KO,104)(E(J),J=JA,JE)
      WRITE(KO,103)
   15 L = JA
      IF (NBOOL . NE . 0)  L=1
      DO 7 I=L,N
      IE = JE
      IF (NBOOL.NE.0)  GO TO 6
      IF (I.LT.JE)  IE=I
    6 WRITE(KO,102)NN(I),(A(I,J),J=JA,IE)
    7 CONTINUE
    8  CONTINUE
      RETURN
      END
```

```
      SUBROUTINE OUTPUT (LCON,NUMBR,NEL)                                OUT
C     CONTROLLING PROGRAM OF OUTPUT    BRANCH                           OUT
C     PRINTS FINAL OUTPUT                                               OUT
      COMMON/SPACE/ZA,ZB,R,N,NHUG,NCON,MULT,KW,KR,KOR,NT,JNT,JCODE,     OUT
     1NPERMS,ND,NFCN,MMAT,N10,NMAT,NE,NPC,LSPARE,MSPARE,ITX,N1,NC1,NC2P,OUT
     2LSRCH,JKW3,LIAR,STEP1,STEP2,EO,NO,MO,IS,A1,A2,EFIN,SAVEA(9),MAD(2)OUT
     3 ,FPARO(2,16),FPAR(2,16),NFPAR(6,16),ITAG( 6),ICTAG(64),          OUT
     4DELT(25),RMAX,RMIN,RSTEP,STEP3                                    OUT
      COMMON/WORK/OVRLAP(42,42),HAMILT(42,42),COET(42,42),COETO(42,42), OUT
     *OLP(42,42),HAM(42,42),E(42),E4(42,6),A,I,J,K,L,M,L1,L2,I7,I6,I5,  OUT
     1BLANK,TAGIT,F(1627)                                               OUT
      COMMON/CIJ/C(16,16),NOTRF,EUGEN(11)                               OUT
      DIMENSION PROD(30) ,TAG(6)                                        OUT
      EQUIVALENCE(PROD,F)                                               OUT
      EQUIVALENCE (IO,LSPARE)                                           OUT
      DIMENSION LCON(NUMBR,NEL)                                         OUT
      SQRTF(X)=SQRT(X)                                                  OUT
 999  DATA (TAG(I),I=1,6)/1H ,1HG,1HU,6HHAMILT,6HOVRLAP,6HTRANS. /      OUT
  305 FORMAT(1H0,20X,A6,1X,6HMATRIX)                                    OUT
  300 FORMAT( //30H  PARAMETERS FOR CONFIGURATION,I3,/ )                OUT
  301 FORMAT(12H    ELECTRON,I3,F11.5,F11.5,3I7,6X,A1)                  OUT
  302 FORMAT(21X,48HDELTA      ZETA        N       M      NU    PARITY    )OUT
 312  FORMAT(14H       ENERGY=,1PE14.7,6H   NE=,I2,/ )                  OUT
  314 FORMAT(1H0,10X,31HENERGIES(ELECTRONIC + NUCLEAR) 24X,21HDISSOCIATIOUT
     1ON ENERGIES / 2(17X,23HHARTREES   ELECT. VOLTS6X,9HKCAL/MOLE) /)  OUT
  315 FORMAT(2(10X,3E15.7))                                             OUT
  320 FORMAT(/ 7X,23HNORMALIZED COEFFICIENTS  )                         OUT
  321 FORMAT  (/7X,12HCOEFFICIENTS  )                                   OUT
 1313 FORMAT(1H0,30X, 55HTHE MONSTER - COURTESY OF KEN WILLIAMS AND EUGEOUT
     *N WELTIN /)                                                       OUT
      WRITE(IO,1313)                                                    OUT
      N1=NMAT                                                           OUT
      N10=N1                                                            OUT
      A=ZA*ZB/R                                                         OUT
      DO 500 I=1,NMAT                                                   OUT
```

```
      E4(I,1)=E(I)+A                                                  OUT
      E4(I,2)=E4(I,1)*27.21                                           OUT
      E4(I,3)=E4(I,1)*627.71                                          OUT
      E4(I,4)=E4(I,1)-A1-A2                                           OUT
      E4(I,5)=E4(I,4)*27.21                                           OUT
  500 E4(I,6)=E4(I,4)*627.71                                          OUT
      DO 54 K = 1,N10                                                 OUT
 54   PROD(K)=0.                                                      OUT
      L2 = NMAT-1                                                     OUT
      DO 55 K=1,N10                                                   OUT
      DO 55 L1 = 1,L2                                                 OUT
      L= L1+1                                                         OUT
      DO 55 M= L,NMAT                                                 OUT
 55   PROD(K)= PROD(K) + 2.*(COET(L1,K)*COET(M,K)*OVRLAP(M,L1))       OUT
      DO 56 K=1,N10                                                   OUT
      DO 56 L=1,NMAT                                                  OUT
 56   PROD(K) = PROD(K)+COET(L,K)**2 *OVRLAP(L,L)                     OUT
      DO 57 K=1,N10                                                   OUT
      DO 57 I=1,NMAT                                                  OUT
      IF(OVRLAP(I,I).GE.0.) GO TO 57                                  OUT
       OVRLAP(I,I)=0.                                                 OUT
 57   COETO(I,K)=(COET(I,K)/SQRTF(PROD(K)))*SQRTF(OVRLAP(I,I))        OUT
C     OUTPUT                                                          OUT
      CALL HDG                                                        OUT
      WRITE(IO,312) EO,NE                                             OUT
      DO 350 I5=1,NCON                                                OUT
      WRITE(IO,300) I5                                                OUT
      WRITE(IO,302)                                                   OUT
      DO 351 I6=1,N                                                   OUT
      I7=LCON(I5,I6)                                                  OUT
      BLANK=TAG(1)                                                    OUT
      IF(MOD(NHUG,2).EQ.0) GO TO 996                                  OUT
      BLANK=TAG(2)                                                    OUT
      IF(NFPAR(4,I7).NE.0) BLANK=TAG(3)                               OUT
  996 WRITE(IO,301)I7,FPAR (1,I7),FPAR (2,I7),(NFPAR (L,I7),L=1,3),BLANKOUT
```

```
  351 CONTINUE                                                    OUT  710
  350 CONTINUE                                                    OUT  720
      WRITE(IO,320)                                               OUT  730
      CALL PMA(COETO,NMAT,F,2,E4(1,1),MSPARE,IO)                  OUT  740
      CALL HDG                                                    OUT  750
      WRITE(IO,314)                                               OUT  760
      WRITE(IO,315)((E4(I,J),J=1,6),I=1,NMAT)                     OUT  770
      CALL HDG                                                    OUT  780
      WRITE(IO,305) TAG(5)                                        OUT  790
      CALL PMA(OVRLAP,NMAT,F ,0,E,MSPARE,IO)                      OUT  800
      WRITE(IO,305) TAG(4)                                        OUT  810
      CALL PMA(HAMILT,NMAT,F ,0,E,MSPARE,IO)                      OUT  820
      WRITE(IO,321)                                               OUT  830
      CALL PMA(COET ,NMAT,F ,2,E ,MSPARE,IO)                      OUT  840
      IF(NOTRF.EQ.0) RETURN                                       OUT  850
      WRITE(IO,305) TAG(6)                                        OUT  860
      CALL PMA(C,NFCN,F,1,F,16,IO)                                OUT  870
      RETURN                                                      OUT  880
      END                                                         OUT  890
•)-PO.CE
```

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